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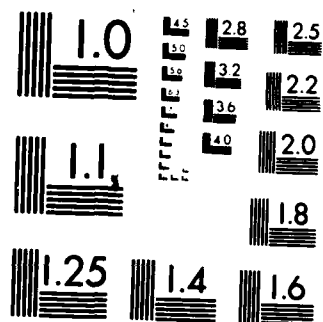
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# STUDY OF NITRATION AND OXIDATION IN OXYNITROGEN SYSTEMS

Final Report

June 1983

By: David S. Ross, Robert J. Schmitt,  
and Ripudaman Malhotra

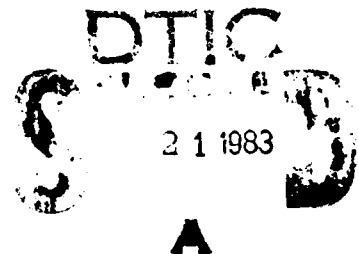
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)			
Nitration	Naphthalene	p-Xylene	Nitric acid
Oxidation	Nitronaphthalene	Sulfuric acid	Radical cation
Electron transfer	Nitronium ion	Trinitrotoluene	Ion-molecule
Nitrosation	Phenol	Nitrogen dioxide	
Electrochemical	Mesitylene	Water	
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)			
<p>Our nitration results consistently demonstrate difficulties with the conventional nitronium ion scheme for mixed acid nitration. Ion molecule studies showed that the Wheland intermediate to aromatic nitration is not formed from the reaction <math>\text{NO}_2^+ + \text{ArH}</math>, but rather from <math>\text{NO}_2^+ + \text{ArH}^+</math>, a result consistent with electron transfer in aromatic nitration. In accord with this observation, we have found that the naphthalene radical cation, prepared independently and isolated as the crystalline salt and dissolved in nitromethane, reacts with <math>\text{NO}_2</math> in that medium to give nitronaphthalene with an o/s ratio of about 50.</p>			

In sulfuric acid media, we have measured directly the rates of nitronium ion formation and its reaction with water over a range of acidities using  $^{14}\text{N}$  nmr spectroscopy. Ours is the first direct determination of the rates, and we find our values to be inconsistent with the conventional nitronium for the special, or  $\text{NO}_2^+$ -catalyzed, nitration of reactive aromatics is incorrect. Thus, prior nitrosation of phenol, naphthalene, mesitylene is not responsible for the accelerated rates. In fact, the latter two compounds do not visibly nitrosate under the conditions that bring about catalyzed nitration; therefore, some other catalytic route involving the lower oxides of nitrogen must be operative.

We also studied reactive aromatic hydrocarbons including mesitylene and p-xylene in fresh,  $\text{NO}_2$ -free acid solution, but in the absence of  $\text{NO}_2$  scavengers such as urea. The results show that the initial nitration rates of these hydrocarbons are significantly lower than accepted values at our acidity. These results, in turn, raise questions specifically about the correctness of the encounter rate nitration model and generally with regard to  $\text{NO}_2^+$  as an intermediate in mixed acid nitration.

In electrochemical studies in nitric acid, we have demonstrated the first electrochemical synthesis of TNT. The process takes place at room temperature in  $\text{NO}_2/\text{HNO}_3$  media.

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## PREFACE

SRI International has conducted a program of research for the Army Research Office under Contract No. DAAG29-80-C0046. The work during the past two and one-half years has included tasks on the fundamentals of the nitration mechanism in both the gas and condensed phases and tasks in electrochemical synthesis of nitroaromatic compounds in strongly acidic media.

The detailed results of this project are presented in 12 appendices, following a summary of important results. Some of the appendices appear as reprints of published journal articles.

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## LIST OF APPENDICES

- A Studies in Aromatic Nitration. Part 2.  $^{14}\text{N}$  NMR Study of the Nitric Acid/Nitronium Ion Equilibrium in Aqueous Sulfuric Acid
- B Catalysis of Nitration of Naphthalene by Lower Oxides of Nitrogen
- C Catalysis of Aromatic Nitration by the Lower Oxides of Nitrogen
- D Studies in Aromatic Nitration. Part 5. Anodic Nitration of Naphthalene
- E Gas Phase Nitration of Aromatic Radical Cations
- F Gas Phase Ion-Molecule Nitration Chemistry: The Nitration of Aromatic Radical Cations by Nitrogen Dioxide
- G On the Mechanism of Oxidation of p-Nitrosophenol by Nitric Acid. Labelling Study Shows the Proposed Nitrodenitrosation Mechanism to be Untenable
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## SUMMARY OF IMPORTANT RESULTS

Aromatic nitration is currently a field of active study, even though the mechanism of the reaction in acid media was considered well established more than three decades ago. Under ARO Contract No. DAAG29-80-C0046, SRI has been studying aromatic nitration. The major features of the work performed over the past two and one-half years include the following:

- The first direct measurements of the rates of nitronium ion formation and the reaction of nitronium ion with water in mixed acid media, and the application of these values over a range of acidities of the mechanism of aromatic nitration.
- The observation that the nitrations of naphthalene and mesitylene in mixed acid media are catalyzed by the lower nitrogen oxides, in a scheme not involving prior nitrosation.
- The observation that the nitrations of p-xylene and mesitylene in sulfuric acid with no  $\text{NO}_x$  scavenger present take place at rates below the accepted literature values by more than an order of magnitude.
- The finding that dinitrotoluene can be nitrated to TNT in  $\text{N}_2\text{O}_5/\text{HNO}_3$  media (white fuming nitric acid) at room temperature and that TNT can be synthesized electrochemically at room temperature in  $\text{HNO}_3/\text{NO}_2$ .
- Demonstration in gas phase ion-molecule work that the even electron system  $\text{NO}_2^+ + \text{ArH}$  does not lead to nitration, but rather undergoes either electron transfer or reaction to phenolic products, whereas the odd electron system  $\text{NO}_2^+ + \text{ArH}^+$  yields the Wheland intermediate for formation of nitroaromatic product.

We have extended the scope of the performance of the nitration reaction and at the same time have broadened the view of the detailed mechanism. Much of the work has demonstrated inconsistencies with the currently accepted nitronium ion scheme for mixed acid nitration. Thus, the measured rates of the reaction of nitronium ion with water are not

consistent with the accepted scheme. Further, the fact that nitration of reactive aromatics, such as mesitylene and naphthalene, is catalyzed by lower nitrogen oxides without prior nitrosation suggests that the operative mixed acid nitration scheme is more complex than is currently accepted. Consistent with these findings is the gas phase ion-molecule work in which nitronium ion does not react with aromatics to provide nitroaromatic product.

We have also developed some new ideas relevant to chemical instrumentation:

- We designed and built a new high pressure ion source for gas phase ion molecule studies.
- We found that in studies of chemical exchange using pulsed FT nmr techniques, the length of the receiver dead time can significantly affect the observed rates.

The work summarized here is described in greater detail in the Appendices included at the end of this report. In some cases, we have reproduced the reprints of published journal articles. We also present material in manuscript form, to be submitted for publication.

# LIST OF PUBLICATIONS

D. S. Ross, K. F. Kuhlmann, and R. Malhotra, "Studies in Aromatic Nitration. 2.  $^{14}\text{N}$  NMR Study of the Nitric Acid/Nitronium Ion Equilibrium in Aqueous Sulfuric Acid," J. Am. Chem. Soc. 1983, 105, 4299-4302.

D. S. Ross, K. D. Moran, and R. Malhotra, "Catalysis of Nitration of Naphthalene by Lower Oxides of Nitrogen," J. Org. Chem. 1983, 48, 2118-2120.

D. S. Ross, G. P. Hum, and W. G. Blucher, "Catalysis of Aromatic Nitration by the Lower Oxides of Nitrogen," J. Chem. Soc. Chem. Comm. 1980, 531-533.

R. J. Schmitt, D. S. Ross, and S. W. Buttrill, Jr., "Gas-Phase Nitration of Aromatic Radical Cations," J. Am. Chem. Soc. 1981, 103, p. 5265-5267.

D. S. Ross, R. Malhotra, and W. C. Ogier, "On the Mechanism of Oxidation of *p*-Nitrosophenol by Nitric Acid. A Labelling Study Shows the Proposed Nitrodenitrosation Mechanism to be Untenable," J. Chem. Soc. Chem. Comm. 1982, 1352-1354.

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## APPENDICES

## Appendix A

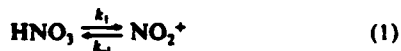
Studies in Aromatic Nitration. 2.<sup>1</sup> <sup>14</sup>N NMR Study of the Nitric Acid/Nitronium Ion Equilibrium in Aqueous Sulfuric Acid

David S. Ross,\* Karl F. Kuhlmann, and Ripudaman Malhotra

*Contribution from the Physical Organic Chemistry Department, SRI International, Menlo Park, California 94025. Received August 11, 1982*

**Abstract:** The nitric acid/nitronium ion equilibrium at 25 °C in aqueous sulfuric acid (81–96%) has been studied by <sup>14</sup>N NMR spectroscopy. In contrast to observations by Seel et al. (1972), who obtained only one NMR signal, we observed separate signals for nitric acid and nitronium ion. A 50% conversion of added nitric acid into nitronium ion is observed in 88% sulfuric acid, a value in good agreement with that obtained by others using Raman spectroscopy. From the line-shape analysis of these spectra, pseudo-first-order rate constants for the formation and hydration of nitronium ion were obtained. Examination of these data reveals certain inconsistencies between the currently accepted mechanism and observed rates and orders of aromatic nitration.

We present here the results of our investigation of nitric acid/nitronium ion equilibrium using <sup>14</sup>N NMR spectroscopy. Our findings reveal inconsistencies between the accepted mechanism and the observed rates and orders of aromatic nitration. The classical studies of Ingold and Co-workers<sup>2</sup> established that nitration of aromatic compounds in nitric acid–sulfuric acid mixtures proceeds through the intermediacy of the nitronium ion (Scheme I), where  $k_1$  and  $k_{-1}$  are respectively the pseudo-first-



order rate constants for the formation and hydration of nitronium ion and  $k_2$  is the specific rate of reaction of the nitronium ion with the aromatic substrate. The formalism used in this paper is that of Moodie, Schofield, and Taylor.<sup>3</sup>

Nitric acid in an acid-catalyzed step is first reversibly transformed into nitronium ion, which then reacts with the aromatic to form products. Such a scheme leads to the following rate expression for the formation of nitro products:

$$\text{rate} = \frac{k_1 k_2 [\text{ArH}] [\text{HNO}_3]}{k_{-1} + k_2 [\text{ArH}]} \quad (3)$$

An independent determination of the rate constants  $k_1$  and  $k_{-1}$  is thus of crucial importance to the mechanism of aromatic nitration.

(1) Part 1: Schmitt, R. J.; Ross, D. S.; Buttrill, S. E., Jr. *J. Am. Chem. Soc.* 1981, 103, 5365–5267.

(2) Ingold, C. K. "Structure and Mechanism in Organic Chemistry"; 2nd ed.; Cornell University Press: Ithaca, NY, 1969.

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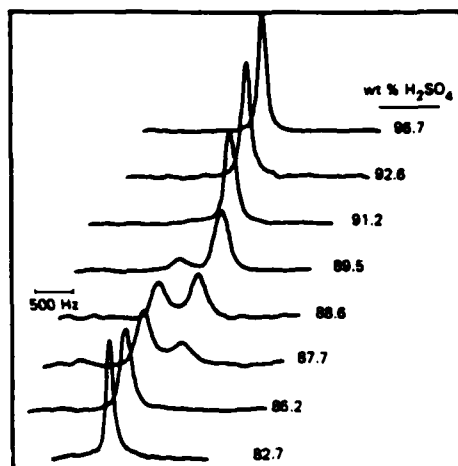


Figure 1.  $^{14}\text{N}$  NMR spectra of 0.5 M solutions of  $\text{HNO}_3$  in aqueous sulfuric acids; (—) offset between spectra = 220 Hz.

Various spectroscopic techniques, including UV<sup>4</sup> and Raman,<sup>5-7</sup> have been used to study equilibrium 1. Chedin performed an extensive Raman spectroscopic study of the nitric and sulfuric acid systems and obtained the fraction of  $\text{N(V)}$  species present as  $\text{NO}_2^+$  over a range of acidities.<sup>5</sup> Later, Zaman confirmed his observations and extended the study to include temperature dependence of the equilibrium.<sup>6</sup>

Although these studies yield information regarding the relative amounts of nitric acid and nitronium ion, they do not furnish rate data. Bunton studied the exchange of label between nitric acid and  $^{18}\text{O}$ -labeled water and determined the rate constant  $k_1$  in aqueous nitric acid.<sup>8</sup> Other attempts at obtaining the estimates of  $k_1$  and  $k_{-1}$  have all been indirect.<sup>3,9,10</sup> These studies have involved measuring the kinetics of nitration of aromatic compounds under a variety of conditions and deconvoluting the kinetic data to obtain values for  $k_1$  and  $k_{-1}$  on the basis of a presumed mechanism for aromatic nitration.

## Results

Recently, Seel et al. examined equilibrium 1 using  $^{14}\text{N}$  NMR spectroscopy.<sup>11</sup> They observed that mixtures of pure nitric acid and sulfuric acids give only one broad  $^{14}\text{N}$  resonance and that the chemical shift of the signal changed with the ratio of the acids. They concluded from this study that the exchange was fast, although no rate data were presented. Also, the signals for solution with  $\text{H}_2\text{SO}_4$  greater than 77 mol % were very broad with half-width at half-height around 200 Hz. Seel investigated the nitric acid-nitronium ion equilibrium along the  $\text{N(V)}\text{--H}_2\text{SO}_4$  axis. Nitrations, on the other hand, are generally performed in solutions that are essentially binary in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{SO}_4$  and to which only a small amount of  $\text{N(V)}$  is added. We therefore decided to study equilibrium 1 along the  $\text{H}_2\text{O--H}_2\text{SO}_4$  axis using  $^{14}\text{N}$  NMR spectroscopy. One potential advantage of such a study would be the direct and independent determination of  $k_1$  and  $k_{-1}$ .

Accordingly, we prepared 0.5 M solutions of  $\text{HNO}_3$  in aqueous sulfuric acids of various strengths and obtained their  $^{14}\text{N}$  NMR spectra at 25 °C. In contrast to the observations by Seel, these

Table I. Rate and Equilibrium Data for the  $\text{HNO}_3/\text{NO}_2^+$  System in Aqueous Sulfuric Acids

% $\text{H}_2\text{SO}_4$	$-\text{H}_0^a$	$-\log a_w$	% $[\text{NO}_2^+]/[\text{N(V)}]$	$\log k_1$ ( $\text{s}^{-1}$ )	$\log k_{-1}$ ( $\text{s}^{-1}$ )
81.0			0		
86.2	8.46	2.96	12	2.26	3.11
87.7	8.68	3.15	34	2.45	2.74
88.6	8.82	3.26	54	2.48	2.41
89.5	8.95	3.36	66	2.59	2.30
91.2	9.21	3.55	92	3.44	2.18
92.6	9.41	3.72	98	3.51	1.91
96.7	10.03		100		

<sup>a</sup> Hammett acidity function.

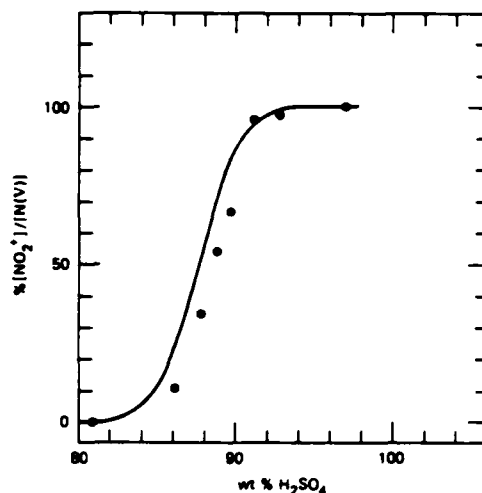


Figure 2. Conversion of  $\text{HNO}_3$  into  $\text{NO}_2^+$  with %  $\text{H}_2\text{SO}_4$ : (—) Raman spectroscopy study, ref 7; (●)  $^{14}\text{N}$  NMR study with  $\text{HNO}_3$ .

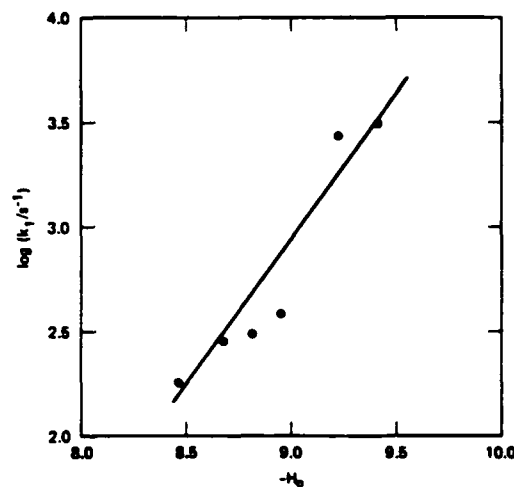


Figure 3. Variation of  $\log k_1$  with  $-\text{H}_0$ :  $d[\log k_1(\text{s}^{-1})]/d(-\text{H}_0) = 1.5 \pm 0.2$ .

solutions gave separate signals for nitric acid and nitronium ion (Figure 1).<sup>12</sup> In sulfuric acid below 85 wt %, only the signal due to nitric acid could be observed. As the acidity was increased, the intensity of that signal decreased, with the simultaneous appearance of another signal; this one is due to nitronium ion. In

(4) Deno, N. C.; Peterson, H. J.; Sacher, E. *J. Phys. Chem.* 1961, 65, 199-201.

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(8) Bunton, C. A.; Halevi, E. A.; Llewellyn, D. R. *J. Chem. Soc.* 1952, 4913-4916.

(9) Chapman, J. W.; Strachan, A. N. *J. Chem. Soc., Chem. Commun.* 1974, 293.

(10) Sheats, G. F.; Strachan, A. N. *Can. J. Chem.* 1978, 56, 1280-1283.

(11) Seel, F.; Hartmann, V.; Gombler, W. Z. *Naturforsch., B* 1972, 27, 325-326.

(12) Ammonium nitrate in aqueous  $\text{H}_2\text{SO}_4$  (85-100%) displays analogous behavior. Chemical shifts on  $\text{HNO}_3$  and  $\text{NO}_2^+$  from the central line of the  $\text{NH}_4^+$  signal, 316 and 226 ppm, respectively, are in good agreement with Seel's results.



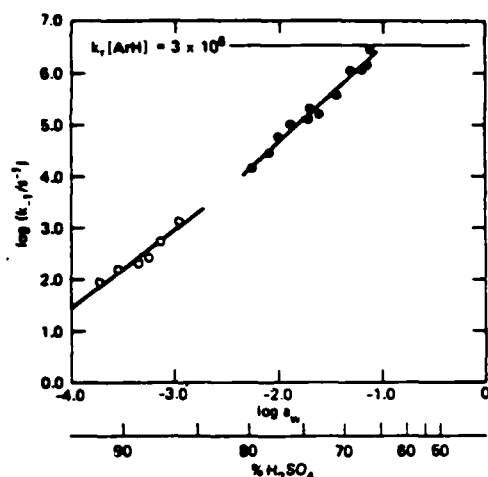


Figure 4. Acidity dependence of the pseudo-first-order rate constant for hydration of nitronium ion ( $k_{-1}$ ): (●) ref 3,  $d(\log k_{-1})/d(\log a_w) = 1.95$ ; (○) this work,  $d(\log k_{-1})/d(\log a_w) = 1.51$ .

solutions of acidities greater than 93%  $H_2SO_4$ , the signal due to nitric acid could not be detected.

The resonances in the intermediate range are broad and suggest a chemical exchange. Line-shape analysis of the spectra yielded the relative amounts of nitric acid and nitronium ion, and also the pseudo-first-order rate constants for the formation and hydration of nitronium ion. These results are presented in Table I.

Figure 2 compares our data for the degrees of conversion of nitric acid into nitronium ion over the range of acidities with those from the most recent Raman spectroscopic study.<sup>7</sup> The two studies are in good agreement, and the point of 50% conversion at 25 °C is at about 88%  $H_2SO_4$ .

Formation of nitronium ion is an acid-catalyzed process. The pseudo-first-order rate constant for this process,  $k_1$ , includes a term that is a measure of the acidity of the medium. The observed first-order rate constant therefore increases with increasing acidity. In Figure 3  $\log k_1$  is plotted against the Hammett acidity function  $H_0$  of the various solutions.<sup>13</sup> The  $H_0$  function is used merely as a convenient acidity scale with no mechanistic implications. The slope of the least-squares line is  $1.5 \pm 0.2$ , which is the same as the value obtained by Moodie, Schofield, and Taylor from their nitration studies.<sup>3</sup> Indeed, the two sets of data lie along the same line.

The first-order rate constant for the hydration of nitronium ion,  $k_{-1}$ , decreases with increasing acidity. This decrease is expected because  $k_{-1}$  is the product of the rate constant for hydration,  $k_{-1}'$ , and some power of  $a_w$ , the activity of water;  $k_{-1} = k_{-1}' a_w^n$ . The value of  $n$  is shown to be about 1.5 from the plot of  $\log k_{-1}$  vs.  $\log a_w$  in Figure 4. Moodie et al.<sup>3</sup> had reported an order of 1.95 in water for the same reaction, albeit in somewhat lower acidities. However, there is a reasonably good agreement between the two sets of data.

The NMR signals due to  $HNO_3$  and  $NO_2^+$  in 88.6%  $H_2SO_4$  coalesce upon warming. Figure 5 shows the temperature dependence of the signals from 14.2 to 43.0 °C. Line-shape analyses of these spectra yield the temperature dependence of  $k_1$  and  $k_{-1}$ . From the Arrhenius plots, activation parameters were obtained:

$$k_1: \Delta H^\ddagger = 14.3 \pm 2.6 \text{ kcal/mol}; \Delta S^\ddagger = 0 \pm 8 \text{ gibbs/mol}$$

$$k_{-1}: \Delta H^\ddagger = 16.8 \pm 2.4 \text{ kcal/mol}; \Delta S^\ddagger = 8 \pm 8 \text{ gibbs/mol}$$

The absence of a large negative entropy of activation for the

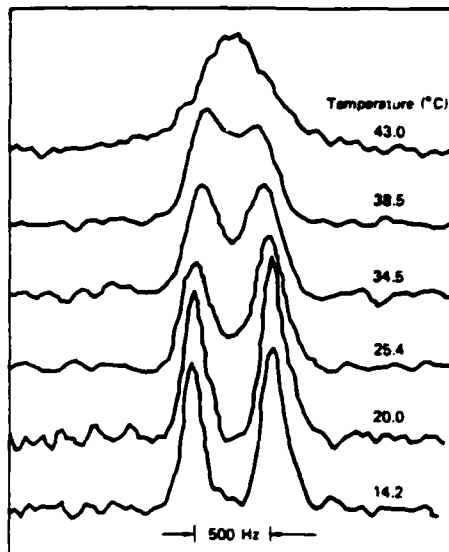


Figure 5. Temperature dependence of  $^{14}N$  NMR of 0.5 M  $HNO_3$  in 88.6%  $H_2SO_4$ .

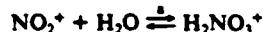
hydration of nitronium ion seems to be inconsistent with a one-step termolecular mechanism (Scheme II) proposed by Moodie et al.<sup>3</sup>

#### Scheme II



and also for the two-step mechanism shown in Scheme III in which step b is rate limiting. However, compensative entropy changes

#### Scheme III



associated with the solvent reorganization could well be large and preclude any definitive conclusion. Thus, on the basis of the present study it is not possible to differentiate between Schemes II and III. We expect to report on this aspect in greater detail in a subsequent paper.

#### Discussion

The close agreement between the rate data for the formation and hydration of nitronium ion as derived from nitration studies by Moodie and co-workers<sup>3</sup> and the rate data obtained by direct NMR measurements suggests that we have provided further evidence for the nitronium ion mechanism for aromatic nitrations. However, as we will demonstrate in this section, both equilibrium and rate data reveal inconsistencies in the mechanism of aromatic nitration.

**Equilibrium Considerations.** Profiles of observed second-order rate constants of nitration of various aromatic substrates show maxima around 90%  $H_2SO_4$ .<sup>13</sup> Vinnik et al.<sup>15,16</sup> showed that, in these strongly acidic media, effects of the media come into play, and if the observed rate constant is corrected by dividing it by the activity coefficient of the aromatic substrate, the profile then exhibits no maximum. The corrected second-order rate constant thus increases steadily with increasing acidity until it finally levels off at a limiting value.

This behavior is easily understood in terms of the nitronium ion mechanism. The increase in the fractional conversion of nitric acid into nitronium ion with increasing acidity results in the increased observed second-order rate constant. But the match

(13) Rochester, C. H. "Acidity Functions"; Academic Press: London, 1970; p 26.

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(15) Vinnik, M. I.; Grabovskaya, Z. E. *Russ. J. Phys. Chem.* 1966, 40, 1221-1223.

(16) Vinnik, M. I.; Grabovskaya, Z. E.; Aromashova, I. N. *Russ. J. Phys. Chem.* 1967, 41, 580-583.

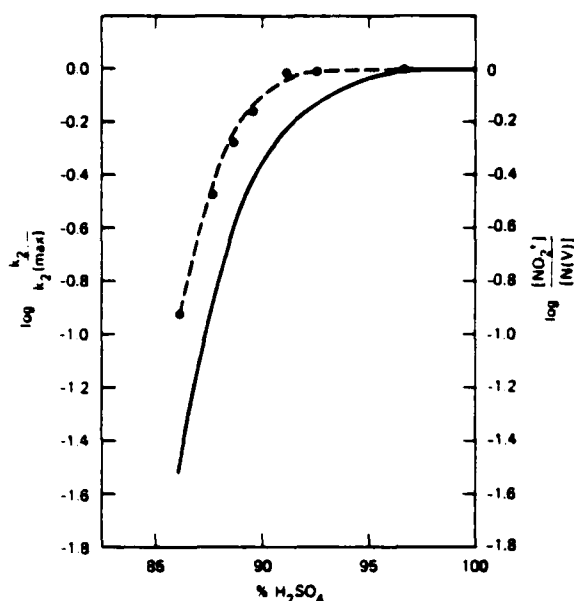


Figure 6. Comparison of the rate profile for nitration of *p*-nitrotoluene and conversion of nitric acid into nitronium ion: (—)  $\log [k_2/k_2(\max)]$ , ref 15; (●)  $\log [NO_2^+]/[N(V)]$ .

is less than perfect. Figure 6 compares the profile of the corrected second-order rate constant for the nitration of *p*-nitrotoluene<sup>15</sup> with the fractional conversion of nitric acid into nitronium ion. As can be seen, the conversion of nitric acid into nitronium ion reaches a limiting value at lower acidities than the rate constant for nitration. Thus in going from 90% to 95%  $H_2SO_4$ , the nitronium ion increases in concentration by about 20% whereas the corresponding nitration rate increases by a factor of 2.3.

**Kinetic Considerations.** The rate expression for the nitration reaction proceeding according to Scheme I is given by eq 3. Under most conditions of nitrations,  $k_{-1}$  is considerably larger than  $k_t[ArH]$  and the rate expression simplifies to eq 4 which explains

$$\text{rate} = \frac{k_1 k_t [HNO_3][ArH]}{k_{-1}} \quad (4)$$

the commonly observed first-order dependence in  $ArH$ . When  $k_{-1} \sim k_t[ArH]$ , a departure from this behavior is expected, and when  $k_{-1}$  is substantially less than  $k_t[ArH]$ , the nitration process should be zero order in aromatic.

$$\text{rate} = k_1 [HNO_3] \quad (5)$$

Indeed, such zero-order behavior in aqueous sulfuric acid has been sought by many investigators but not found, although a departure from strict first-order behavior has been observed.<sup>3</sup> Lack of zero-order dependence of  $ArH$  for even such reactive aromatics as anisole ( $k_t = 6 \times 10^4 M^{-1} s^{-1}$ ) at concentrations of  $5 \times 10^{-3} M$  is inconsistent with the values of  $k_{-1}$  as projected by our study

and also with those in the literature.<sup>3</sup> Also presented in Figure 5 are the values of  $\log k_{-1}$  calculated from the work of Moodie et al.<sup>17</sup> The two sets of data span different regions of acidity, but agreement between them can be inferred by the fact that a smooth curve could adequately fit both sets of data. From Figure 5 it is seen that  $k_{-1} = 3 \times 10^6 s^{-1}$  for about 65%  $H_2SO_4$ . At 72%  $H_2SO_4$ ,  $k_{-1}$  is  $3 \times 10^5 s^{-1}$ , a value considerably less than  $k_t[ArH] \sim 3 \times 10^4 s^{-1}$ . Under these conditions, if Scheme I were operative, zero-order nitration in anisole should have been observed.

Given  $k_{-1}$  and the fact that zero order in aromatic was not observed, we can estimate an upper limit for the value of  $k_t$  at any given acidity. In 80%  $H_2SO_4$ , with  $[anisole] = 9.9 \times 10^{-3} M$ , we find that  $k_t \leq 1.3 \times 10^4 M^{-1} s^{-1}$ , or at least two orders of magnitude less than the expected bimolecular rate coefficient for encounter between two species in this medium. This discrepancy raises a serious question about the validity of Scheme I on the basis of the hypothesis of encounter rate control for the nitration of anisole. It should be pointed out that including an extra step (encounter pair formation or electron transfer) does not resolve the discrepancy. We suggest that a reinvestigation of the kinetics of mechanism of aromatic nitrations is in order.

#### Experimental Section

Stock sulfuric acid solutions were prepared by diluting reagent grade sulfuric acid (98.6 wt %). The acidity of each of these diluted acids was determined by alkalimetry with a Metrohm Potentiograph Model E436 titrator.  $HNO_3$  (100%) was obtained by distillation from oleum under reduced pressure and was kept frozen until just before use. The NMR tubes were sealed under vacuum and stored in a dry ice/acetone bath. The  $^{14}N$  NMR spectra were recorded on a Varian Model FT 80A instrument equipped with an external  $^1H$  lock and a temperature controller. Generally 25 000 transients were accumulated with pulse widths of 30  $\mu s$  and an acquisition time of 10 ms. Acoustic ringing in the probe caused an undulating base line. For line-shape analyses, the program was modified to include a quadratic and a linear term for the base line. This treatment adequately corrected the base line. The reported percent  $H_2SO_4$  of each solution is the titrimetric value that has been corrected for the formation of water and consumption of  $H_2SO_4$  according to eq 6. The Hammett acidities are those due to Ryabova et al.<sup>18</sup> The



activity of water data were obtained by interpolation of data given in the International Critical Tables.<sup>19</sup>

**Acknowledgment.** Support for this work under United States Army Research Office Contract No. DAAG29-80-C-0046 is gratefully acknowledged. We acknowledge very helpful discussions with Professor Roy Moodie and we also wish to thank Dr. J. Shoolery of Varian Associates, Palo Alto, for his help in recording the NMR spectra.

Registry No. Nitric acid, 7697-37-2; nitronium ion, 14522-82-8.

(17) Moodie et al. reported only the  $k_1/k_2$  ratio, which is equal to  $k_{-1}/k_t$ . If  $k_t$  is known,  $k_{-1}$  can be calculated.

(18) Ryabova, R. S.; Medvetskaya, I. M.; Vinnik, M. I. *Russ. J. Phys. Chem.* 1966, 40, 182.

(19) "International Critical Tables", McGraw-Hill Book Company, Inc.: New York, 1933; Vol. III, p 303.

## Appendix B

**Catalysis of Nitration of Naphthalene by Lower  
Oxides of Nitrogen<sup>1</sup>**

**Summary:** Nitrous acid catalyzed nitration of naphthalene does not proceed through nitrosation, and the mechanism

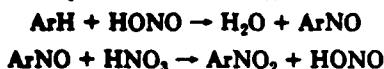
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(1) Part 4 of the series *Studies in Aromatic Nitration*. Part 3: Ross, D. S.; Malhotra, R.; Ogier, W. C. *J. Chem. Soc., Chem. Commun.* 1982, 1353.

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is best understood in terms of a chain reaction involving naphthalene radical cation.

Sir: Nitrous acid ( $\text{NO}^+$ ,  $\text{N(III)}$ ) can play contrasting roles in aromatic nitrations. It acts as an anticatalyst in the nitration of most aromatics in nitromethane/nitric acid mixtures and in nitric acid alone. On the other hand, in nitric acid/sulfuric acid mixtures it catalyzes the nitration of substrates such as phenol, aniline, and other aromatics activated toward electrophilic substitutions.<sup>2</sup> This catalytic effect has been classically explained through initial nitrosation, followed by oxidation to the corresponding nitroaromatic by nitric acid<sup>3</sup> ( $\text{N(V)}$ ).



Recently Giffney and Ridd<sup>4</sup> reported a mechanism for nitrous acid catalyzed nitration of *N,N*-dimethylaniline in about 85% sulfuric acid not proceeding through C-nitrosation. A key step in the proposed mechanism involves the oxidation of the aromatic by  $\text{NO}^+$  and the formation of *N,N*-dimethylaniline radical cation. Under conditions of lower acidities, however, these authors admit that the reaction could proceed by prior nitrosation. More recently Main, Moodie, and Schofield<sup>5</sup> have shown the reaction of 1,2,3-trimethoxy-5-nitrobenzene with nitric acid in 60–70% sulfuric acid to be also catalyzed by nitrous acid in a manner analogous to the nitration of *N,N*-dimethylaniline.

We have previously shown that nitrous acid catalyzes the nitration of phenol by a mechanism not involving prior nitrosation.<sup>6</sup> However, since phenol undergoes nitrosation, it was not possible to study the kinetics of  $\text{N(III)}$ -catalyzed nitration proceeding with no nitrosation as distinct from the component proceeding by nitrosation followed by oxidation. We required as a substrate an aromatic hydrocarbon that would be subject to special nitration but not undergo nitrosation. We report here the results of our study of the nitrous acid catalyzed nitration of naphthalene, which proceeds under conditions where naphthalene does not nitrosate.

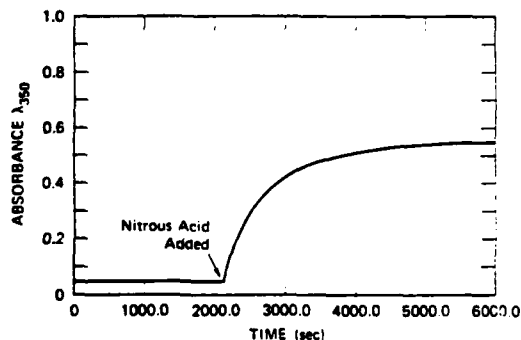


Figure 1. Effect of nitrous acid on the nitration of naphthalene in 55.9%  $\text{H}_2\text{SO}_4$ : naphthalene,  $1.31 \times 10^{-4}$  M; nitric acid,  $1.30 \times 10^{-2}$  M; nitrous acid,  $6.56 \times 10^{-3}$  M.

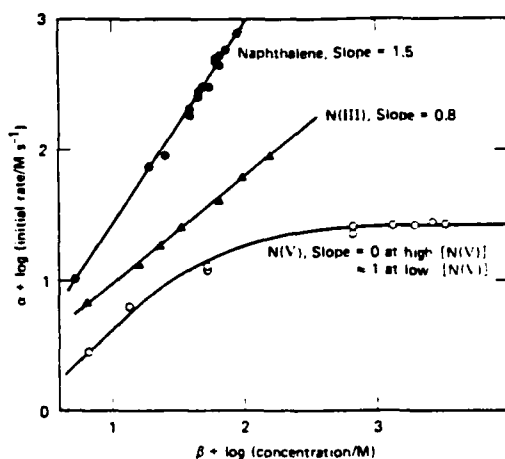
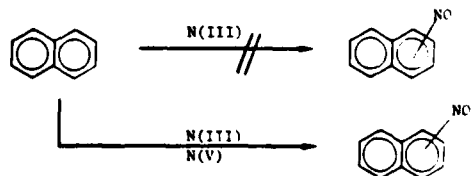


Figure 2. Variation of the initial rate of nitration of naphthalene in 60.4%  $\text{H}_2\text{SO}_4$  at 25 °C with various reactants. (●) Naphthalene:  $\alpha = 9.38$ ;  $\beta = 5.74$ ; nitric acid,  $1.30 \times 10^{-2}$  M; nitrous acid,  $3.30 \times 10^{-3}$  M. (▲)  $\text{N(III)}$ :  $\alpha = 8.58$ ;  $\beta = 6.00$ ; nitric acid,  $1.30 \times 10^{-2}$  M; naphthalene,  $1.31 \times 10^{-4}$  M. (○)  $\text{N(V)}$ :  $\alpha = 8.65$ ;  $\beta = 4.98$ ; nitrous acid,  $3.30 \times 10^{-3}$  M; naphthalene,  $1.31 \times 10^{-4}$  M.

In all runs the additions of  $\text{N(III)}$  and  $\text{N(V)}$  were as aliquots of aqueous solutions of the respective sodium salts. Thus for the reactions with  $\text{N(V)}$ , initially the solutions were free of lower oxide species. Below 60% sulfuric acid the nitration rate for naphthalene in such media is very slow, as is shown in Figure 1. However, as is also shown in the figure, the addition of a small quantity of nitrous acid dramatically brought about a very rapid nitration. The conversion is quantitative and the identity of the products was confirmed by GC and HPLC. The  $\alpha/\beta$  isomer ratio was determined to be  $25 \pm 3$ . In contrast, if the same quantity of nitrous acid were added to a similar solution without  $\text{N(V)}$ , the naphthalene was observed to be unchanged after 80 min. The rate of nitrosation is thus below 3% /h.

The promotion of nitration by  $\text{N(III)}$  is considered to be related to the change in product  $\alpha/\beta$  ratio with the purposeful addition of  $\text{N(III)}$ ,<sup>2</sup> and as stated above the reaction route was considered to be prior nitrosation followed by oxidation of the nitrosoaromatic. However, our observations here suggest such a model to be incorrect; here we have a clear case of catalysis by  $\text{N(III)}$  not involving prior nitrosation.



To understand the mechanism of the catalysis, we investigated the kinetics of the reaction in 56.4%  $\text{H}_2\text{SO}_4$ . To assure that the results applied to a homogeneous condition, we first determined that the absorbances of naphthalene in the solutions prior to the addition of oxynitrogen species followed Beer's law ( $\epsilon_{276} 5390 \text{ M}^{-1} \text{ cm}^{-1}$ ). The fit was satisfactory up to the upper limit of the concentration range of the study, and the slight deviation at higher concentrations could well be due to some association of the dissolved hydrocarbon, although this factor was not confirmed. Several kinetic runs were conducted in which the concentrations of nitric and nitrous acids were held constant at  $1.3 \times 10^{-2}$  and  $3.3 \times 10^{-3}$  M, respectively, while the naphthalene concentration was varied between  $9.7 \times$

(2) Hoggett, J. G.; Moodie, R. B.; Penton, J. R.; Schofield, K., "Nitration and Aromatic Reactivity" Cambridge University Press: London, 1971.

(3) Bunton, C. A.; Hughes, E. D.; Ingold, C. K.; Jacobs, D. I. H.; Jones, T. H.; Minkoff, G. J.; Reed, R. J. *J. Chem. Soc.* 1950, 2828.

(4) (a) Giffney, J. C.; Ridd, J. H., *J. Chem. Soc. Perkin Trans. 2*, 1979, 618. (b) Al-Omar, F.; Fujiwara, K.; Giffney, J. C.; Ridd, J. H.; Robinson, S. R. *Ibid.* 1981, 518.

(5) Main, L.; Moodie, R. B.; Schofield, K., *J. Chem. Soc., Chem. Commun.* 1982, 48.

(6) Ross, D. S.; Hum, G. P.; Blucher, W. G. *J. Chem. Soc., Chem. Commun.* 1980, 532.

$10^{-6}$  and  $1.4 \times 10^{-4}$  M. None of these runs gave good first-order or second-order plots, and we therefore obtained the order of the reaction in naphthalene by analyzing the initial rates ( $r_i$ ) as shown in Figure 2. By this method the order in naphthalene was determined to be 1.5. This surprising result was verified by reexamination of the full kinetic runs, which were found to fit plots for a reaction 1.5 order in naphthalene. These results are in contrast to those of Ridd and Co-workers,<sup>4</sup> who found N(III)-catalyzed nitration of *N,N*-dimethylaniline to be first order in the aromatic. This finding is moreover obviously not in accord with the prenitrosation scheme.

The order of nitration in nitrous acid was also determined by the method of initial slopes and found to be 0.8 for the range of nitrous acid concentrations between  $6.7 \times 10^{-6}$  and  $1.7 \times 10^{-4}$  M (Figure 2). The order with respect to nitric acid changed in the range of concentrations studied. The reaction was zero order in nitric acid when the concentration of nitric acid was above  $6.3 \times 10^{-3}$  M. Below  $10^{-4}$  M nitric acid, the order was approximately 1. Variation of the log initial rate with log initial nitric acid concentration is also shown in Figure 2.

From these kinetic data we can draw some conclusions regarding the mechanism of the reaction. The order of 1.5 in naphthalene can be explained in terms of a chain mechanism in which both initiation and propagation steps are first order in naphthalene. The changing order in nitric acid indicates a change in the rate-limiting step with changing N(V) concentration. We stipulate that nitric acid is involved in a propagation step following the step in which naphthalene is consumed. Zero order in nitric acid for high concentrations is consistent with the electron-transfer oxidation scheme of Ridd and co-workers,<sup>4</sup> and recently Main, Moodie, and Schofield<sup>6</sup> found evidence for such a limiting kinetic form in the case of nitrous acid catalyzed nitration of 1,2,3-trimethoxy-5-nitrobenzene.

Further support for electron transfer is provided by the results of electrochemical nitration of naphthalene. Ebersson et al.<sup>7</sup> and Achord and Hussey<sup>8</sup> reported that controlled potential electrolysis of naphthalene at +1.3 V (vs. Ag/Ag<sup>+</sup>) in the presence of  $N_2O_4$  produces nitronaphthalenes with an  $\alpha/\beta$  isomer ratio of  $23 \pm 3$ , a value we have been able to reproduce, but significantly different from that reported by Perrin.<sup>9</sup>

However, the order of 1.5 in naphthalene cannot be reconciled with a simple scheme involving oxidation by  $NO^+$ , followed by reaction with  $NO_2$ . We support the idea of electron transfer being an important step, but the overall scheme must include a chain. So far we have not been able to identify the  $NO_2$  species involved in the reaction, primarily because at the acidity we have worked, several of the  $NO_2$  species are present in significant quantities, including  $NO$ ,  $HONO$ ,  $NO^+$ ,  $NO_2$ ,  $N_2O_4$ ,  $NO_3^-$ , and  $HNO_3$ .<sup>9</sup> We are currently studying the acidity dependence of N-(III)-catalyzed nitration of naphthalene, with the hope to establish the identity of the oxidant and develop a detailed mechanism. However, it is clear that the nitration of simple hydrocarbons can be complex and the role of the lower nitrogen oxides can be significant.

**Acknowledgment.** We acknowledge the generous support of the U.S. Army Research Office. We also thank Professor R. B. Moodie for helpful discussion.

Registry No. Naphthalene, 91-20-3; nitrous acid, 7782-77-6.

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Received January 27, 1983

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(8) Achord, J. M.; Hussey, C. L. *J. Electrochem. Soc.* 1981, 128, 255-261.

(9) Perrin, C. L. *J. Am. Chem. Soc.* 1977, 99, 5516.

(10) Ross, D. S.; Gu, C. L., to be published.

**Appendix C**

**Catalysis of Aromatic Nitration by the Lower Oxides of Nitrogen**

**By DAVID S. ROSS,\* GEORGINA P. HUM, and WILLIAM G. BLUCHER**  
**(S.R.I. International, 333 Ravenswood Avenue, Menlo Park, CA 94025)**

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## Catalysis of Aromatic Nitration by the Lower Oxides of Nitrogen

By DAVID S. ROSS,\* GEORGINA P. HUM, and WILLIAM G. BLUCHER  
(S.R.I. International, 333 Ravenswood Avenue, Menlo Park, CA 94025)

**Summary** In the absence of nitrous acid traps, the nitration of phenol in 56.2% sulphuric acid displays autocatalytic behaviour; on the other hand, the isomer ratio of the products is inconsistent with the commonly accepted prior nitrosation scheme, and some other route for the promotion of nitration must be operative.

We report here on anomalous nitration patterns of phenol in mineral acid nitration media which suggest an unusual catalysis of the nitration. Such nitrations of phenol and other substrates activated toward electrophilic substitution are recognized to be subject to the catalytic effects of nitrous acid and perhaps other lower oxides of nitrogen, and the mode of action is assumed to be prior nitrosation followed by oxidation of the nitrosoaromatic.<sup>1</sup> We have found that this reaction scheme is not necessarily operative, or, at the very least, is not alone in promoting nitration.

We used phenol at 25 °C in 56.2% sulphuric acid with no added nitrous acid trap. Aliquots of sodium nitrate and nitrite solutions served as fresh sources of the N<sup>V</sup> and N<sup>III</sup> species, respectively, in each run.<sup>†</sup> We added the two oxyacids to phenol-sulphuric acid solutions either alone or sequentially, with 30 s between additions. The reactions were quenched and worked up after either 30 s or 7 min total reaction time. The analyses were carried out by h.p.l.c., and the data are presented in the Table.

oxidation of the nitroso compound by addition of N<sup>V</sup> was isolated and found to have an *o*:*p* ratio of (0.03 ± 0.02):1.

Next, in run 3 we see that with only N<sup>V</sup>, after 7 min the nitration is effectively complete, in contrast with the 30 s result of run 1. Clearly some sort of catalysis is operative in the 7 min run, since from our measured initial rate constant for phenol nitration in these media ( $k_{\text{no}} = 3.9 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) only about 7% of the phenol should have been nitrated over that period. This value is in fair agreement with the value for nitration at that acidity in studies with added HONO traps.<sup>1b</sup> However, the product *o*:*p* ratio is 0.78:1, a value clearly inconsistent with a prior nitrosation route, which should yield an *o*:*p* ratio of about 0.03:1.

Finally, in accord with this assessment is the result of run 4 in which N<sup>V</sup> was added 30 s before N<sup>III</sup>. While small in an absolute sense, the product *o*:*p* ratio of (0.11 ± 0.01):1 shows that 3–4 times more *ortho* nitration is taking place in this mixture than would be expected from the essentially pure prior nitrosation route operative in run 5.

If we assume that in run 3 both nitrosation and nitration are proceeding in parallel, then, given the nitrosation *o*:*p* ratio of 0.03:1, and recognizing that the *o*:*p* ratio for straight nitration is about 2.0:1,<sup>1b</sup> it can be shown that the observed product mixture can be obtained only if the nitration rate is about 1.9 times greater than the rate of

TABLE. Nitration of phenol in 56.2% sulphuric acid at 25 °C\*

Run	Mode	Reaction time	Nitrophenol <sup>b</sup> (%)	Ratio <i>o</i> : <i>p</i>	Material balance <sup>c</sup> (%)	Remarks
1	N <sup>V</sup> alone	30 s	< 1	—	98	98% phenol recovered
2	N <sup>III</sup> alone <sup>d</sup>	30 s	quantitative (nitrosophenol)	—	—	—
3	N <sup>V</sup> alone	7 min	87	0.78	87	No phenol observed in product
4	N <sup>V</sup> first <sup>e</sup>	7 min	96 <sup>+</sup>	0.11 ± 0.01	98	No phenol observed in product
5	N <sup>III</sup> first <sup>e</sup>	7 min	96 <sup>+</sup>	0.03 ± 0.02	98	No phenol observed in product

\* The volume of the solutions was 3.3 ml. Initial concentrations: N<sup>V</sup>, 6.1–9.7 × 10<sup>-3</sup> M; phenol, 6.1 × 10<sup>-3</sup> M; N<sup>III</sup>, 6.1 × 10<sup>-3</sup> M. Analyses on quenched samples by h.p.l.c. <sup>b</sup> Fraction of starting phenol converted into nitrophenols. <sup>c</sup> Fraction of starting phenol accounted for. <sup>d</sup> Performed in a spectrophotometer; no product isolated. <sup>e</sup> Both N<sup>III</sup> and N<sup>V</sup> added. Second component added 30 s after first.

First, we see that whereas the intervention of NO<sub>2</sub> catalysis of phenol nitration can bring about autocatalysis,<sup>1</sup> in the brief 30 s period employed in run 1 almost no nitration took place.

We then established that, in accord with work of Challis and Lawson, phenol nitrosation is rapid and yields almost entirely the *para*-isomer.<sup>2</sup> In our work the conversion was complete and quantitative within 30 s (run 2), with a measured second-order rate constant of  $k_{\text{no}} = 93 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . A measure of the very small degree of substitution was obtained from runs, shown collectively as run 5, in which the nitrophenol formed from the subsequent

nitration *via* nitrosation and oxidation. In addition, since the reaction is complete in 7 min, a lower limit can be calculated for the apparent second-order rate constant for the catalysed component of the aromatic nitration,  $k_{\text{no}}^{\text{cat}} > 5.0 \times 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

This value is an order of magnitude greater than that for the conventional nitration, and clearly a potent catalyst not involving nitrosation is operative. It is not clear if in fact the reaction is truly catalysed or merely promoted, and we use the former term here with reservation.

The chemistry in effect here must be elucidated. It can be suggested that phenol may be a special case, since at

<sup>†</sup> The oxidation states of the oxyacids of nitrogen are used here because more than one specific form is present for both nitrous and nitric acids in 50–60% sulphuric acid. Thus, N<sup>III</sup> in these solutions is both NO<sup>+</sup> and HONO; N<sup>V</sup> is both HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup>.

least in acetic anhydride its nitration is more sensitive to promotion by the lower nitrogen oxides than that of anisole.<sup>4</sup> On the other hand, our results can be compared with those recently presented by Giffney and Ridd,<sup>5</sup> who suggest that the lower oxides of nitrogen play a non-nitroactive role in the reaction of *NN*-dimethylaniline in nitration media. Their proposed scheme includes electron transfer from the protonated substrate to  $\text{NO}^+$ , followed by

radical cation reactions. The possibility of radical cation intermediates in aromatic nitration more generally has been recently raised,<sup>6</sup> and it seems the entire question of nitration mechanism is yet to be resolved.<sup>6</sup>

We acknowledge the support of this research by the Army Research Office and Lawrence Livermore Laboratories

(Received, 8th February 1980; Com. 124.)

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<sup>2</sup> B. C. Challis and A. J. Lawson, *J. Chem. Soc. (B)*, 1971, 770.

<sup>3</sup> J. C. Giffney and J. A. Ridd, *J. Chem. Soc., Perkin Trans. 2*, 1979, 618.

<sup>4</sup> J. G. Hoggett, R. B. Moodie, and K. Schofield, *Chem. Commun.*, 1980, 605.

<sup>5</sup> C. L. Perrin, *J. Am. Chem. Soc.*, 1977, 99, 5510; L. Ebersson, L. Johnson, and F. Radner, *Acta Chem. Scand., Ser. B*, 1978, 32, 749.

<sup>6</sup> R. G. Coombes in 'Comprehensive Organic Chemistry,' Vol. 2, ed. I. O. Sutherland, Pergamon, Oxford, 1979, p. 309.



## Appendix D

### STUDIES IN AROMATIC NITRATION. PART 5. ANODIC NITRATION OF NAPHTHALENE

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#### Introduction

In attempts to confirm or deny the relevance of electron transfer processes during nitration of reactive aromatics several investigators have studied the reaction of independently generated aromatic radical cation with  $N_2O_4/NO_2$ .<sup>1-6</sup> Perrin provided support for the one-electron transfer process by showing that controlled potential electrolysis of naphthalene in the presence of  $N_2O_4$  at potentials positive enough to yield naphthalene radical cation, but insufficient for  $NO_2$  oxidation, gave nitronaphthalenes as product. The  $\alpha/\beta$  isomer ratio of the product nitronaphthalene was  $9 \pm 1$ , a value very similar to that obtained for mixed acid nitration of naphthalene in the presence of urea. In the absence of urea, catalysis by lower oxides of nitrogen results in nitronaphthalenes with an  $\alpha/\beta$  ratio of  $20 \pm 2$ .<sup>5,7</sup>

Following Perrin's work, other investigators reported the anodic nitration of naphthalene, but have obtained an  $\alpha/\beta$  ratio of  $25 \pm 2$ .<sup>2,3,8</sup> Perrin's low ratio remains unduplicated. An analysis of the current yield of product as a function of time led Eberson to suggest that the nitration reaction observed by Perrin was probably due to anodically generated acid.

Eberson et al.<sup>3</sup> showed that the naphthalene radical cation will react with  $N_2O_4$ . In that work crystalline hexafluorophosphate salt of

naphthalene radical cation was prepared electrochemically and suspended in  $\text{CH}_2\text{Cl}_2/\text{N}_2\text{O}_4$ . The product ratio obtained in the heterogeneous system was  $\alpha/\beta = 45 \pm 5$ .

We have conducted similar studies in an attempt to clarify the issue, particularly with respect to the presence of water in the system, and the ratio of nitronaphthalenes that can result from the homogeneous reaction of  $\text{NO}_2$  with naphthalene radical cation.

### Results and Discussion

With the exception of the radical cation salt work, all the previous electrochemical studies were conducted in acetonitrile, a solvent which is very difficult to dry thoroughly. Trace amounts of water present in the solvent react with  $\text{N}_2\text{O}_4$  to give nitrous and nitric acids. A UV-Vis spectrum of  $5 \times 10^{-3}$  M  $\text{N}_2\text{O}_4$  (the concentration used by Perrin) in rigorously dried<sup>9</sup> acetonitrile showed the characteristic bands of nitrous acid. In our hands, even the most scrupulous drying failed to provide acetonitrile that would not give HONO after addition of  $\text{N}_2\text{O}_4$ . From the ratio of the peak to valley absorbances, we deduced that the content of  $\text{N}_2\text{O}_4$  could not be greater than 5% in these dried solutions. In more concentrated solutions, 0.1 M  $\text{N}_2\text{O}_4$  in acetonitrile, a greater fraction of  $\text{N}_2\text{O}_4$  remained, but HONO was still present.

When nitrous acid was observed in the UV-Vis spectrum, we found it not possible to carry out electrolysis at +1.3 V versus  $\text{Ag}/\text{Ag}^+$  (0.1 M) because of the oxidation of  $\text{NO}_2^-$  to  $\text{NO}_2$  occurs at +0.95 V. Nonetheless, electrolysis at the lower potential resulted in the formation of nitronaphthalenes with an  $\alpha/\beta$  ratio of  $25 \pm 3$ .

In response to Ebersson's criticism that nitronaphthalenes arise from an acid catalyzed process, Perrin suggested that the presence of water in his system, which was not rigorously dried, reduced the acidity to a point that such acid catalyzed processes could not take place.<sup>10</sup> We studied the effect of water on the isomer ratio by deliberately adding water to the anodic solution. However, as shown in the table, there was no change in the isomer ratio of product nitronaphthalenes.

Table 1<sup>a</sup>EFFECT OF WATER ON THE ISOMER RATIO IN ELECTROCHEMICAL  
NITRATIONS OF NAPHTHALENE

Potential vs Ag/Ag <sup>+</sup>	Solvent	HONO Present	H <sub>2</sub> O Added $\mu$ L	$\alpha/\beta$ ratio
+1.3	CH <sub>3</sub> CN	Yes	None	22 $\pm$ 3
+1.3	CH <sub>3</sub> CN	Yes	200	20 $\pm$ 3
+1.3	CH <sub>2</sub> Cl <sub>2</sub>	No	None	27 $\pm$ 3

<sup>a</sup>All reactions used tetrabutylammonium tetrafluoroborate as the supporting electrolyte. All runs were at 25°C.

We conclude that HONO was a complicating factor in all the reported electrochemical work in CH<sub>3</sub>CN. In methylene chloride, however, our UV-Vis spectra showed only N<sub>2</sub>O<sub>4</sub>, and even at 10<sup>-3</sup> M N<sub>2</sub>O<sub>4</sub> HONO was not observed. We conducted electrolyses in methylene chloride solutions whose anhydrous nature was tested by the absence of bands due to HONO in the UV-Vis spectra. In these cases a slightly higher  $\alpha/\beta$ -nitro-naphthalenes ratio of 27 was found. This result is probably not significantly different from the results in CH<sub>3</sub>CN.

We wished to test whether the heterogeneous nature of the reaction of naphthalene radical cation salt and NO<sub>2</sub> as performed by Eberson<sup>3</sup> affected the product ratio. We therefore synthesized the hexafluorophosphate salt at -45°C in methylene chloride, dissolved it in nitromethane and then added a HONO free solution of N<sub>2</sub>O<sub>4</sub> in methylene chloride to it. An  $\alpha/\beta$  ratio of 55  $\pm$  0 was found for this fully homogeneous reaction.

### Conclusions

We have found that, even in thoroughly dried solutions of  $\text{CH}_3\text{CN}$ , HONO is always found after the addition of  $\text{N}_2\text{O}_4$  to the solution. HONO is known to catalyze nitrations of reactive aromatics such as naphthalene. The addition of water to solutions of  $\text{N}_2\text{O}_4$ , naphthalene,  $\text{CH}_3\text{CN}$  and electrolyte did not affect the  $\alpha/\beta$ -nitronaphthalene ratio significantly. A homogeneous solution of  $\text{N}_2\text{O}_4$  and a salt of the naphthalene radical cation gave a very high a/b ratio which should be representative of the effect of a radical cation intermediate on the selectivity observed in aromatic nitrations.

### Experimental

All experiments were performed using a PARC 173 potentiostat/galvanostat equipped with a PARC model 179 digital coulometer. The UV-Vis spectra were recorded on a HP 8450A UV-Vis spectrophotometer. Tetrabutylammonium tetrafluoroborate was used as the supporting electrolyte for all experiments except those involving synthesis of naphthalene radical cation salts, where tetrabutylammonium hexafluorophosphate was used. All experiments were done in a divided cell with dried methylene chloride or dried acetonitrile as the solvent, platinum electrodes and  $\text{Ag}/\text{Ag}^+$  (0.1 M) as the reference electrode.

Crystalline naphthalene-hexafluorophosphate was synthesized by literature methods<sup>3</sup>. Following the synthesis, the electrode with the crystals still attached was carefully removed from the solution. Under a stream of argon, the crystals were scraped from the electrode into nitromethane. A solution of  $\text{N}_2\text{O}_4$  in methylene chloride, checked for the absence of HONO contamination by UV-Vis, was slowly added with stirring. The reaction was quenched by addition of water, worked up and analyzed by gas chromatography. A Varian model 3700 gas chromatograph with a fused silica capillary column coated with SE 30, 100 ft by 0.025 inch was used for all analyses.

### Acknowledgement

Support for this work under the U.S. Army Research Office (Contract No. DAAG29-80-C-0046) is gratefully acknowledged.

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## Appendix E

### Gas-Phase Nitration of Aromatic Radical Cations

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The possibility that radical cations may be intermediates in aromatic nitrations is a subject of current debate. For aromatics

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which are more easily oxidized than toluene. Perrin<sup>1</sup> has suggested that an initial electron transfer takes place in the reaction of nitronium ion with the aromatic, followed by recombination of the resulting  $\text{NO}_2^+/\text{ArH}^+$  pair. Perrin studied the nitration of naphthalene in acetonitrile solvent in the anodic compartment of an electrochemical cell and found the same ratio of  $\alpha$ - and  $\beta$ -nitronaphthalene products as that produced by nitric acid nitration in acetonitrile.<sup>1</sup> However, Ebersson et al. question this result and suggest that the electrochemical nitration observed by Perrin was a homogeneous, acid-catalyzed process mediated by traces of protic substances in the acetonitrile.<sup>2</sup> Further questions were raised by Draper and Ridd when they found that the radical cation of mesitylene generated by  $\text{Ce(IV)}$  was nitrated on both the ring and the methyl carbons, in contrast to the pure ring nitration by nitric acid under the same conditions.<sup>3</sup>

In this paper, we report the first direct observation of the reaction of an aromatic radical cation with  $\text{NO}_2$  and the formation of a  $\sigma$ -bonded intermediate product. Our research was performed by using a new high-pressure mass spectrometer to study the gas-phase reactions of the odd-electron species  $\text{NO}_2^+$  and benzene radical cation. Earlier gas-phase work was done by Ausloos and Lias, who studied the even-even  $\text{NO}_2^+/\text{ArH}$  systems and observed only charge transfer and oxygen atom transfer.<sup>4</sup>



Their studies were performed at pressures of about  $10^{-5}$  torr in an ion cyclotron resonance spectrometer. In agreement with earlier work,<sup>5</sup> they were able to form the "nitration" product  $\text{ArHNO}_2^+$  only by transfer of  $\text{NO}_2^+$  from species such as  $\text{CH}_3\text{ONO}_2^+$ , but no information on the structure of the product was obtained.<sup>4,7</sup> Moreover, under these conditions, the formation of the  $\text{ArHNO}_2^+$  product was favored for aromatic systems containing electron-withdrawing substituents, in distinct contrast to the common experience in condensed phase nitrations.

Our work uses a flow discharge mass spectrometer of a unique design. Reactions are run in a 1.27-cm i.d.  $\times$  17-cm stainless steel tube with 10 torr of helium and 0.5 torr of argon as the buffer gas. Ions are generated by a pulsed discharge in a flowing argon atmosphere that functions as an argon flash lamp. The lamp is isolated from the helium and all reactive neutrals by an open-ended glass tube through which the flow of argon enters the ion source. The argon resonance radiation ionizes species with an ionization potential of less than 12 eV down the full length of the flow tube. The ion source is sampled by a pinhole orifice; the ions are then mass analyzed by an extramolecular quadrupole mass filter and pulse counted by an electron multiplier. This lamp is pulsed at about 100 Hz. Ion concentration vs. time data are recorded by using a Digital Equipment Corporation LSI 11/2 processor in a VT103 terminal. The buffer gas concentration is about  $4 \times 10^{17}$  molecules/cm<sup>3</sup>, reactive neutral concentrations are about  $10^{13}$  molecules/cm<sup>3</sup>, and the ion concentration is about  $10^8$  ions/cm<sup>3</sup>. The gas velocity is about 2000 cm/s, and the helium flow rate is about 15 atm cm<sup>3</sup>/s.<sup>8</sup>

(1) Perrin, C. L. *J. Am. Chem. Soc.* 1977, 99, 5516-5518.

(2) Ebersson, L.; Jonsson, L.; Radaer, F. *Acta Chem. Scand., Ser. B* 1978, 32, 749-753.

(3) Draper, M. R.; Ridd, J. H. *J. Chem. Soc., Chem. Commun.* 1978, 445-446.

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(5) (a) Banerji, S. A.; Hoffman, M. K.; Burney, M. M. *J. Am. Chem. Soc.* 1978, 92, 7501-7502. (b) Dunbar, R. C.; Shen, J.; Olah, G. A. *Ibid.* 1972, 94, 6862-6864. (c) Hoffman, M. K.; Burney, M. M. *Tetrahedron Lett.* 1971, 2539-2542.

(6) Dunbar, R. C.; Shen, J.; Olah, G. A. *J. Am. Chem. Soc.* 1972, 94, 6862-6864.

(7) For gas-phase nitration studies, see: Reents, W. D., Jr.; Frieser, B. S. *J. Am. Chem. Soc.* 1980, 102, 271-275.

(8) As a test of the establishment of thermal equilibrium within the ion source, the equilibrium constant was measured as a function of temperature for the dimerization (eq 2). Values of  $\Delta G = 14.7$  kcal/mol and  $\Delta S = 22.5$  eu were obtained, which are in good agreement with the literature values of  $\Delta G = 15.06$  kcal/mol and  $\Delta S = 23.18$  eu. (a) Jasinski, J. M.; Rosenfeld, R. N.; Golden, D. M.; Brannan, J. L. *J. Am. Chem. Soc.* 1979, 101, 2259-2265. (b) Anich, V. G.; Bowers, M. T. *Ibid.* 1974, 96, 1279-1286. (c) Field, F. H.; Hamlet, P.; Libby, V. F. *Ibid.* 1969, 91, 2839-2842.

We find that when a mixture of benzene,  $\text{NO}_2$ , helium, and argon is ionized, rapid electron transfers during the first 0.25 ms yield the aromatic radical cation.<sup>9</sup> Equilibrium 2 is then established, giving predominantly the dimer. The product ion



$\text{C}_6\text{H}_6\text{NO}_2^+$  readily forms from the reaction of the dimer with  $\text{NO}_2$  (eq 3).



$$k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

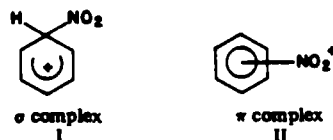
Also observed are two other primary products,  $\text{C}_6\text{H}_6\text{NO}^+$  and  $\text{C}_6\text{H}_6\text{O}^+$ . The former arises from the reaction of  $\text{NO}$ , present as an impurity, with the radical cation dimer (eq 4). The  $\text{C}_6\text{H}_6\text{O}^+$



$$k = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

ion is formed only at short times by the reaction 1b, consistent with the earlier ICR results.<sup>4</sup>

In order to probe the structure of the nitration product  $\text{C}_6\text{H}_6\text{NO}_2^+$ , we studied a mixture of benzene- $d_6$ ,  $\text{NO}_2$ , and tetrahydrofuran (THF). Because the proton affinity (PA) of THF (PA = 196.4 kcal/mol) is greater than that of nitrobenzene (PA = 191.6 kcal/mol)<sup>10</sup> and assuredly greater than the PA of any  $\sigma$ -bonded intermediate that might be formed, deuteron transfer from  $\text{C}_6\text{D}_6\text{NO}_2^+$  to THF would establish that the reaction of the aromatic radical cation with  $\text{NO}_2$  gives a  $\sigma$ -bonded product (structure I or O-protonated nitrobenzene). However, a  $\pi$  complex (II) would not be able to transfer a deuteron (proton) to THF because this structure lacks acidic protons. Benzene- $d_6$  was used

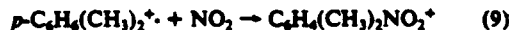


to eliminate any possible confusion about the source of the proton (deuteron) transferred in the reaction. Neither  $\text{C}_6\text{D}_6^+$  nor  $(\text{C}_6\text{D}_6)_2^+$  transferred a deuteron to THF in control experiments (eq 5 and 6). The proton transfer (7) readily took place, dem-



onstrating the  $\sigma$ -bonded character of the product. Similar results were found with pyridine (PA = 218 kcal/mol) as the base.

We have also studied the nitration of the toluene and *p*-xylene radical cations (eq 8 and 9). Both of these reactions occur via



$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

the monomer of the aromatic cation unlike the benzene reaction (eq 3) which goes only by the dimer of the radical cation. Thus, we are not observing a simple exchange of ligands in the reaction complex, but rather a direct reaction between an aromatic radical cation and  $\text{NO}_2$ .

While the present results prove that the nitration product contains a  $\sigma$  bond between the  $\text{NO}_2$  and the aromatics, they cannot distinguish between structure I and O-protonated nitrobenzene. No evidence has been found for formation of a  $\pi$  complex in this study. This is in contrast to nitrosation reactions, either Frieser and Reents' work on  $\text{C}_6\text{H}_6 + \text{CH}_3\text{ONO}^+$  or our own studies of

(9) Since  $\text{IP}(\text{NO})$  and  $\text{IP}(\text{NO}_2) > \text{IP}(\text{C}_6\text{H}_6)$ .

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$C_6H_5^{\cdot+} + NO$ ,<sup>11</sup> where only a  $\pi$  complex is formed with no evidence for a  $\sigma$  complex.

We believe this to be the first clear example of a reaction of an aromatic radical cation with  $NO_2$  to produce a nitroaromatic species. We have also observed similar reactions for other aromatic radical cations. While solvation effects may change, in some cases, the relative stabilities of the radical cation and  $NO_2^+$ , these results show that further consideration is warranted of the aromatic radical cation as an intermediate in nitration reactions.

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(11) Unpublished results.



Appendix F

GAS PHASE ION-MOLECULE NITRATION CHEMISTRY:  
THE NITRATION OF AROMATIC RADICAL CATIONS BY  
NITROGEN DIOXIDE

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Abstract: We have observed that aromatic radical cations readily nitrate by addition of  $\text{NO}_2$  in the gas phase. Nitronium ion,  $\text{NO}_2^+$ , is found to react by electron transfer and by  $\text{O}^+$  transfer to aromatics. Aromatic radical cations that are electron rich or electron deficient are found to nitrate either slowly or not at all, whereas the benzene radical cation and other aromatic radical cations readily nitrate. The effects of clustering of the aromatic radical cation on nitration are discussed and compared with nitration in solution.

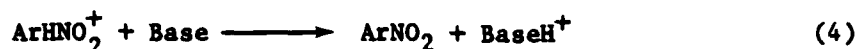
## Introduction

We recently reported our preliminary results<sup>1</sup> on the gas phase ion-molecule chemistry of aromatic radical cations reacting with nitrogen dioxide. This account describes the full details of the study and further results concerning the mechanism of aromatic nitration. To our knowledge, the gas phase ion chemistry of these odd electron systems has not been previously reported.

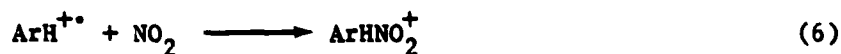
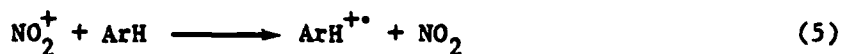
The generally accepted mechanism for aromatic nitration in solution is shown in eqs (1) through (4):<sup>2</sup>



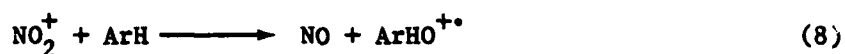
$\sigma$ -complex



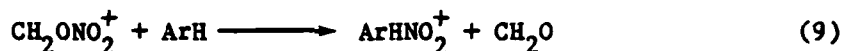
Nitronium ion is first formed by protonation of nitric acid in an acidic medium. The ion reacts with the aromatic to yield an association complex, which isomerizes to a  $\sigma$ - (or Wheland-) intermediate, which then gives up a proton to the medium to yield the nitroaromatic product. A  $\pi$ -complex is invoked to explain the selectivity observed in this reaction<sup>3</sup> although the nature of the complex is still not agreed upon.<sup>2a</sup> For aromatics that are more easily oxidized than toluene, Perrin<sup>4</sup> has suggested electron transfer takes place in the reaction of nitronium ion with the aromatic, followed by a recombination of the resulting  $\text{NO}_2/\text{ArH}^{+\bullet}$  pair.



In earlier gas phase work on aromatic nitration, researchers studied the even-even electron  $\text{NO}_2^+/\text{ArH}$  systems and observed only charge transfer and oxygen atom transfer from nitronium ion.<sup>5,8</sup>

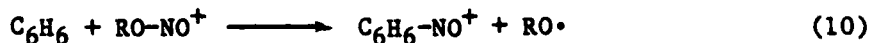


These studies were both done at  $10^{-5}$  torr in an ICR spectrometer. Nitration of aromatics was accomplished only when nitronium ion was bound, as in  $\text{CH}_2\text{ONO}_2^+$ .



No information on the structure of the product ion was obtained. Moreover, under these conditions, the formation of  $\text{ArHNO}_2^+$  product was favored for aromatic systems containing electron-withdrawing substituents, in distinct contrast to the common experience in condensed phase nitrations.

Finally, Reents and Frieser<sup>9</sup> have investigated the nitrosation of benzene in the gas phase, with a nitrite ester as the source of  $\text{NO}^+$ .



From a study of proton transfer and IR spectral results, they determined that the product (eq 10) was a  $\pi$ -complex rather than a  $\sigma$ -complex. Their result is consistent with condensed phase studies in which nitrosation of benzene gives only a reversible  $\pi$ -complex, not a  $\sigma$ -complex. We have also studied the reactions of aromatic radical cations with  $\text{NO}^1$  and have observed results in agreement with Reents and Frieser, obtaining only a reversible  $\pi$ -complex as the product.

## Experimental Procedures

A block diagram of the flow discharge mass spectrometer used for these experiments is shown in Figure 1. The helium carrier/buffer gas is purified by passage through a liquid-nitrogen-cooled 0.75-inch-OD copper trap filled with Davidson 3A molecular sieves. The reactive neutrals are mixed with the helium in a vacuum line by bleeding small quantities of the neutrals through a Whitey RS22 stainless steel metering valve. The premixed helium/neutral gas flow enters the upstream end of a 0.5-inch-OD by 6-inch-long flow tube. Generally, 10 to 15 torr of helium and 0.01 torr of the reactive neutrals are used. This gives a helium/argon concentration of  $10^{17}$  molecules  $\text{cm}^{-3}$ , reactive neutrals at approximately  $10^{14}$  molecules  $\text{cm}^{-3}$ , and a ion density of approximately  $10^8$   $\text{cm}^{-3}$ . The ion source can be used at pressures from 5 to 100 torr and over a temperature range of 30° to 200°C. The mass spectrometer region is differentially pumped by 6-inch diffusion pumps equipped with cold traps in both the ion-focusing and quadrupole regions. This provides adequate pumping capacity to handle pressures up to 100 torr in the ion source with a sampling orifice of 100  $\mu\text{m}$ .

A small argon flash lamp is used as a photoionization source for the mass spectrometer. The design of the ion source is shown in Figures 2 and 3. The flash lamp is an open-ended, 1/8-inch-OD Pyrex tube into which a 1/16-inch-OD, two-hole ceramic insulator has been inserted. Two 10-mil molybdenum wires protrude about 1/16 inch beyond the end of the insulator and about 1/8 inch from the opening of the glass tubing (Figure 3). A steady flow of argon is maintained in the flash lamp, contributing approximately 0.5 torr to the total pressure in the ion source. The lamp is pulsed at about 100 Hz at a potential of 2500 V using a simple spark gap.

On pulsing, excited argon atoms and argon ions are produced. The argon ions are lost to the walls of the glass tube while the excited argon atoms give off photons of 11.6 and 11.8 eV, ionizing anything with an IP below 11.8 eV throughout the length of the flow tube. Hence a plug of gas from the end of the Pyrex tube to the sampling orifice is ionized. The mixture of neutrals and ions is sampled as it flows past

the sampling orifice. The neutrals are pumped away, and the ions are mass analyzed and recorded as a function of elapsed time since the argon lamp flash.

Housing the electrodes within the Pyrex tubing prevents pyrolysis of the reactive neutrals by shielding them from the high energy pulses. Pressure in the ion source is measured by an MKS Baratron Model 220-BHS, 0.100 torr. Most of the gas flow is exhausted to a 200 L min<sup>-1</sup> Leybold-Heraeus pump with a small fraction being sampled through a 100- $\mu$ m orifice.

The ion signal is focused into the quadrupole via a series of lenses. Two flat plates are followed by a set of quadrupole focusing lenses to steer the ion beam, and then two more flat plates are used to direct the beam into the quadrupole. The ion source is held at +25 V. Mass discrimination effects are minimized, but the ion signals are not corrected for these effects.

Mass analysis is done with a Extranuclear quadrupole with 5/8 inch rods. The signal is then collected, ion counted, and analyzed in a DEC VT 105 terminal equipped with an LSI 11/2 microprocessor. The data are recorded on either an X-Y plotter or a line printer. For the time-resolved data, data points are taken every 100  $\mu$ s after the start pulse for a period up to 5 ms, the maximum residence time of ions in the flow tube.

We performed experiments using the benzene radical cation-dimer system to check whether the ions in the source were at thermal equilibrium. An example of our results is shown in Figure 4. Previous work established a  $\Delta H = -14.7$  kcal mole<sup>-1</sup> and a  $\Delta S = -22.5$  eu for the reaction.<sup>10</sup> We have measured this equilibrium at six temperatures ranging from room temperature up to 150°C and calculated a  $\Delta H = -15.0$  kcal mol<sup>-1</sup> and a  $\Delta S = -23.2$  eu, which are in good agreement with the literature values.

Materials. We used helium (99.999%), and argon (99.9995%), NO 99.99%. NO<sub>2</sub> was purified by distilling the cylinder gas into a 10-l storage bulb; then several freeze/thaw cycles were employed to remove the lower oxides of nitrogen. The bulb was then pressurized with oxygen and allowed to stand for a week to remove the remaining NO. The oxygen was pumped off, the NO<sub>2</sub> pressure was measured, and the bulb was pressurized with helium to dilute the NO<sub>2</sub>. Despite these precautions, evidence of nitrosation (presumably due to some NO impurity or possibly formed by photolysis of NO<sub>2</sub> by the argon resonance radiation) was always observed. The organics for his study were obtained from commercially available sources and were distilled into the system from lithium aluminum hydride or calcium hydride whenever possible. Toluene-d<sub>3</sub> (99% D) and toluene-d<sub>8</sub> (99.5% D) were obtained from Stohler Isotope Chemical, and benzene-d<sub>6</sub> (99.5% D) was obtained from Aldrich Chemical Company.

Rate Constant Calculation. The rate of reaction of a radical cation or any other ion, A<sup>+</sup>, with a neutral is described by:

$$-d[A^+]/dt = k[A^+][N] \quad (11)$$

where k is the bimolecular rate constant in cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Because [N] = 10<sup>14</sup> molecules cm<sup>-3</sup> and [A<sup>+</sup>] ~ 10<sup>8</sup> ions cm<sup>-3</sup>, pseudo-first-order kinetics apply. The reactive neutral concentration, N, is calculated at room temperature as

$$N = \frac{(P_{\text{He}})(3.26 \times 10^{16})(F_N)}{F_{\text{He}}} \quad (12)$$

where

$P_{\text{He}}$	= Pressure of the helium buffer gas (torr)
$3.26 \times 10^{16}$	= Number of particles cm <sup>-3</sup> torr <sup>-1</sup>
$F_N$	= Flow of the reactive neutral (atm cm <sup>-3</sup> s <sup>-1</sup> )
$F_{\text{He}}$	= Flow of the helium buffer gas (atm cm <sup>-3</sup> s <sup>-1</sup> )

Thus, the second-order rate constant is calculated from

$$k = \frac{-d\ln[A^+]}{dt} \frac{F_{\text{He}}}{(P_{\text{He}})(F_N)(3.26 \times 10^{16})} \quad (13)$$

The helium flow and pressure and the flow of the neutral are measured by their pressure change in a calibrated volume. The  $d\ln[A^+]/dt$  term is obtained from the slope of a plot of  $\ln[A^+]$  versus time. We assume that the cross-sectional ion density in the flow tube is of the plug-flow type rather than the laminar flow encountered in a flowing afterglow; hence, the average ion velocity should be the same as the buffer gas velocity.<sup>11</sup> Therefore, the term alpha, which is normally used to correct for the increased flow velocity of the ions in a flowing afterglow, is neglected for this calculation.<sup>11</sup>

### Results

To explore the scope of reaction (14),



we examined the gas phase ion chemistry of the radical cations of 18 aromatic compounds with  $\text{NO}_2$ . The results are summarized in Table I. The highly activated naphthalene cation reacted only very slowly with  $\text{NO}_2$  while the highly deactivated tetrafluorobenzenes showed no detectable ( $k < 10^{-13} \text{ cm}^3 \text{ reaction molecule sec}$ ) reaction.

All the aromatic radical cations tested react with NO to give nitrosoaromatic products.



This nitrosation result parallels that of Reents and Frieser,<sup>9</sup> who nitrosated a wide variety of compounds and obtained a set of relative nitroso affinities.

In addition to nitration and nitrosation products, phenolic products are observed for every aromatic tested. These products result from the reactions of nitronium ion with the aromatic (eq 8). They are not a product of aromatic radical cation reactions (see below).

Table 1  
REACTIONS OF AROMATIC RADICAL CATIONS  
WITH NO<sub>2</sub> AND NO<sup>a</sup>

ArH	Nitration via Aromatic Radical Cation	$k$ (cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup> ) <sup>b</sup>
C <sub>6</sub> H <sub>6</sub>	Yes	2.4 x 10 <sup>-11</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	Yes	1.2 x 10 <sup>-11</sup>
<i>p</i> -C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	Yes	1.7 x 10 <sup>-11</sup>
Mesitylene <sup>c</sup>	Yes	--
1,2,4-Trimethylbenzene	Yes	--
Phenol	Yes	--
C <sub>6</sub> H <sub>5</sub> F	Yes	3.7 x 10 <sup>-11</sup>
C <sub>6</sub> H <sub>5</sub> Cl	Yes	--
<i>o</i> -C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	Yes	--
<i>m</i> -C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	Yes	1.2 x 10 <sup>-12</sup>
<i>p</i> -C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	Yes	2.9 x 10 <sup>-12</sup>
1,2,4-C <sub>6</sub> H <sub>3</sub> F <sub>3</sub>	Yes	--
1,2,3,4-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	No	--
1,2,4,5-C <sub>6</sub> H <sub>2</sub> F <sub>4</sub>	No	--
Furan	No	--
Pyridine	No	--
<i>m</i> -FC <sub>6</sub> H <sub>4</sub> CF <sub>3</sub>	Yes	--
Naphthalene	Very slow	--

<sup>a</sup>Nitration by NO<sub>2</sub><sup>+</sup> results in ArHO<sup>+</sup> or electron transfer as product, eq 7 and 8.

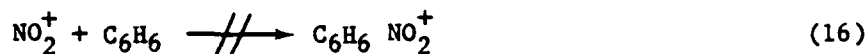
<sup>b</sup>Forward rate constant for ArH<sup>+</sup> includes ArHNO<sup>+</sup> (from NO impurity).

<sup>c</sup>See discussion for explanation of unusual behavior.



## Discussion

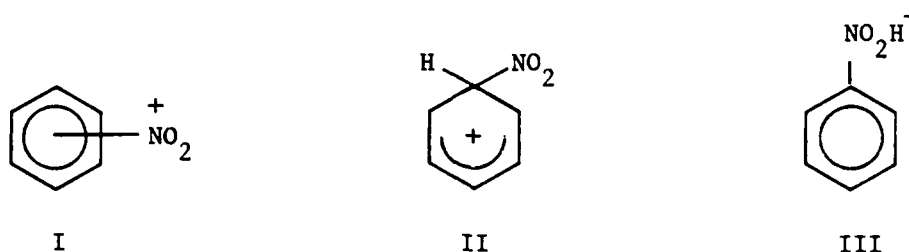
Role of Nitronium Ion in Gas Phase Nitrations. In mixed acid nitrations, nitronium ion,  $\text{NO}_2^+$ , is believed to be the nitrating agent (eq 1 through 4). From our results, which are consistent with the results of Ausloos and Lias<sup>6</sup> obtained at lower pressures, we found that  $\text{NO}_2^+$  does not nitrate aromatics in the gas phase, but instead reacts by either  $\text{O}^+$  or electron transfer (eqs 16 through 18):



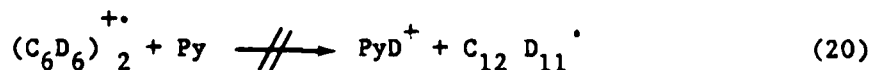
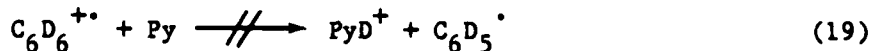
This result is clearly illustrated in Figures 5(a) and 5(b). Figure 5(a) shows a time-resolved plot of the reaction of  $\text{NO}_2^+$  with *p*-xylene. The  $\text{NO}_2^+$  concentration decays exponentially via electron transfer from or via  $\text{O}^+$  transfer to *p*-xylene with a rate constant of  $2.0 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . Figure 5(b) shows a time-resolved plot of the formation of the nitrated xylene coming from the xylene radical cation. The much lower formation of protonated nitroxylene ion from the xylene radical cation does not begin until the vast majority of  $\text{NO}_2^+$  is consumed (nitration is slower than either electron transfer or  $\text{O}^+$  transfer). Thus, we can rule out  $\text{NO}_2^+$  as the nitrating agent in these gas phase experiments.

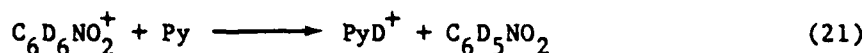
Product Structure. It has been proposed that the reaction of an aromatic radical cation with  $\text{NO}_2$  should give a  $\sigma$ -complex rather than a  $\pi$ -complex (*vide supra*). The earlier ion-molecule work did not address the question of the structure of the nitration product,  $\pi$ - or  $\sigma$ -complex.<sup>5-8</sup>

To probe the structure of the benzene nitration product  $C_6H_6NO_2^+$ , we studied a mixture of benzene- $d_6$ ,  $NO_2$ , and a base, pyridine (Py). Because the proton affinity (PA) of Py (PA = 218 kcal mol $^{-1}$ )<sup>12</sup> is greater than that of nitrobenzene (PA = 191.6 kcal mol $^{-1}$ )<sup>12</sup> and assuredly greater than the PA of any  $\sigma$ -bonded intermediate that might be formed, deuteron transfer from  $C_6H_6NO_2^+$  to Py would establish that the reaction of an aromatic radical cation with  $NO_2$  gives a  $\sigma$ -bonded product (structure II or III). However, a  $\pi$ -complex (I) would not transfer a deuteron (proton) to Py because this structure lacks acidic protons.



Benzene- $d_6$  was used to eliminate any possible ambiguity in the source of the proton (deuteron) transferred in the reaction. Neither  $C_6D_6^{+\bullet}$  nor  $(C_6D_6)_2^{+\bullet}$  transferred a deuteron to Py in control experiments (eqs 19 and 20). The only product from the  $C_6D_6^{+\bullet}$ /Py reaction is a strongly bound  $(C_6D_6-Py)^{+\bullet}$  cluster. When a mixture of  $C_6H_6$ /Py/ $NO_2$  was ionized, rapid deuteron transfer to pyridine was observed from the product of the reaction of  $C_6D_6^{+\bullet} + NO_2$ . Figure 6, shows a time-resolved plot of the reaction, shows  $C_6D_6^{+\bullet}$ , rapidly dimerizes to  $(C_6D_6)^{+\bullet}$ , which reacts with  $NO_2$ . The  $C_6D_6NO_2^+$  ion then proton transfers to Py to give  $PyD^+$ , which dimerizes to give  $Py_2D^+$ . Other cluster products,  $(C_6D_6-C_5H_5N)^+$  and  $C_5H_5N-C_6D_6NO_2)^+$ , are also shown in Figure 6. The deuteron transfer (equation (19) eliminates structure I as the product. We cannot distinguish between structures II and III, but the only pathway to III is through II.

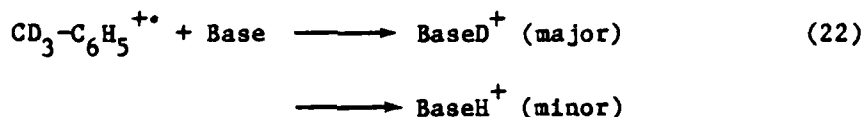




Similar results were obtained when tetrahydrofuran ( $\text{PA} = 196 \text{ kcal mol}^{-1}$ )<sup>12</sup> was used.

The benzene radical cation readily reacts with NO to nitrosate and give the  $\text{C}_6\text{D}_6\text{NO}^+$  ion. In a manner similar to that described above, we tested for the type of complex formed. Here, ionization of a mixture of  $\text{C}_6\text{D}_6/\text{NO}/\text{Py}$  resulted in no deuteron transfer to pyridine. Thus, we conclude that the  $\text{C}_6\text{D}_6\text{NO}^+$  ion is a  $\pi$ - rather than a  $\sigma$ -complex. Our result from the open-shell electron reaction parallels the result found by Reents and Frieser in their studies of closed-shell electron shell nitrosations.<sup>9</sup>

In a similar manner, we also attempted to determine whether aromatic radical cations nitrate on the ring or at the side chain in the gas phase. As stated above, solution studies involving the nitration of mesitylene via  $\text{NO}_2$  and  $\text{Ce(IV)}$  as an electron transfer reagent have shown that a considerable amount of the reaction proceeds via side chain nitration.  $\alpha,\alpha,\alpha$ -Toluene- $\text{d}_3$  was chosen for these studies because it readily nitrates and forms the radical cation dimer only slowly. Unfortunately, the toluene radical cation is acidic enough to proton transfer to bases that are basic enough to accept a proton from the expected protonated nitrotoluene product (eq 22).



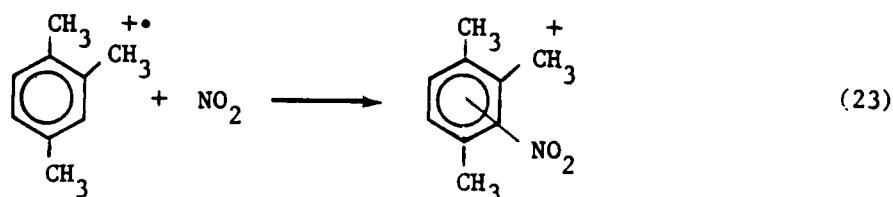
We can, however, determine whether the bulk of the reaction is at the ring or side chain. The results obtained from reaction of the toluene radical cation with pyridine in the absence and presence of  $\text{NO}_2$  are compared below.

System	PyD <sup>+</sup> /PyH <sup>+</sup>
C <sub>6</sub> H <sub>5</sub> CD <sub>3</sub> <sup>+</sup> /Py	2/1
C <sub>6</sub> H <sub>5</sub> CD <sub>3</sub> <sup>+</sup> /Py/NO <sub>2</sub>	1/4

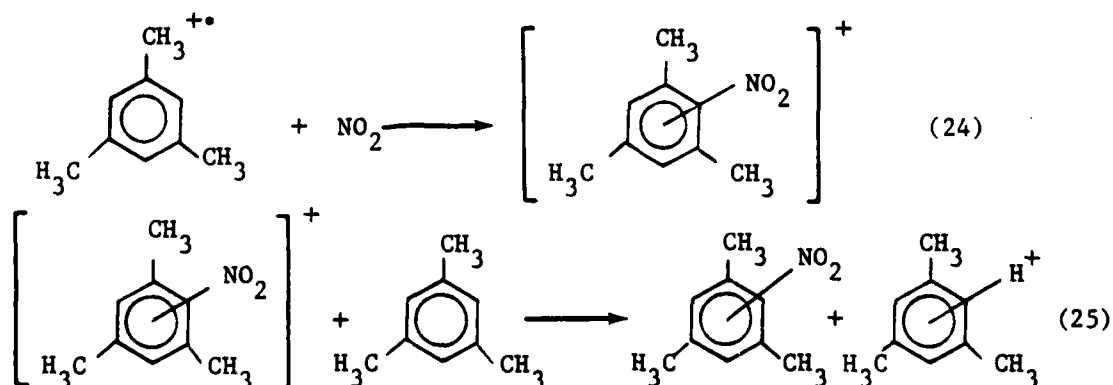
The large difference between the PyD<sup>+</sup>/PyH<sup>+</sup> ratios for products of these reactions shows that the nitration is predominantly at the ring rather than on the side chain.

Nitration of Mesitylene, 1,2,4-Trimethylbenzene, and Napthalene.

We have observed surprising differences in the reactivity of the radical cations of mesitylene and 1,2,4-trimethylbenzene to NO<sub>2</sub>. The 1,2,4-trimethylbenzene radical cation is readily nitrated (eq 23) to give a nitroaromatic cation.



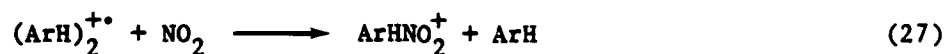
Mesitylene behaves somewhat differently. The mesitylene radical cation readily adds NO<sub>2</sub> to give a short-lived nitromesitylene cation (eq 24 and 25). However, the nitromesitylene cation is not stable in this environment, losing a proton to mesitylene to give protonated mesitylene as the product.



The proton loss from mesitylene is quite unexpected because we assumed that the proton affinity of nitromesitylene (2-nitro-1,3,5-trimethylbenzene) would be greater than that of mesitylene because proton affinity tends to increase with increasing functionality. We also expected the proton affinities of mesitylene and 1,2,4-trimethylbenzene or those of nitromesitylene and 5-nitro-1,2,4-trimethylbenzene to be approximately equal and the behavior of these two trimethylbenzene systems to parallel to each other. Because of the observed proton transfer from IV to mesitylene, we believe that we are observing a lower than expected proton affinity for 2-nitro-1,3,5-trinitrobenzene that results from steric crowding of the nitro group.

The behavior of naphthalene is also somewhat unexpected. Naphthalene nitrates very slowly. Thus, naphthalene should nitrate easily, in analogy to the ease with which it nitrates in solution, or at least behave similarly to mesitylene or 1,2,4-trimethylbenzene, which are also electron-rich systems. This failure of naphthalene to readily nitrate is still not understood.

Effect of Clustering on Reaction. Many aromatic radical cations rapidly cluster with a neutral aromatic molecule. For example, the benzene radical cation clusters with a neutral benzene with an equilibrium constant of approximately  $K_{eq} \sim 10^6$  at 25°C. We have observed that the nitration<sup>1</sup> of aromatic radical cations proceeds whether or not the radical cation dimerizes.



We do not believe that the dimer is required for the nitration reaction, but frequently the dimer formation is so rapid that the dimerization is complete before nitration can occur. For benzene, in which the equilibrium constant for dimerization is very high, we cannot tell if the monomer reacts at all with  $\text{NO}_2$ , with apparently all the reaction

coming from the dimer. However, for *p*-xylene, for which the monomer can be easily made with little or no dimer, the reaction is observed to proceed from only the monomer. In the case of fluorobenzene, both the monomeric and dimeric forms lead to nitroaromatic product.

Comparison with Solution Chemistry. Some comparisons and contrasts can be drawn between the solution and the gas phase results. It is not surprising that a highly deactivated aromatic such as tetrafluorobenzene, do not nitrate in the gas phase; the same behavior is observed in solution. In solution, a difluoroquinone is the product instead of a nitroaromatic, whereas in the gas phase no reaction is observed. It is surprising that a highly activated aromatic, such as naphthalene, nitrates slowly in the gas phase. Indeed, in analogy with solution results, one would expect the reaction to occur on every collision. The gas phase results on clustered nitronium ion by Lias and Ausloos<sup>9</sup> parallel our observations on both deactivated and activated aromatics. While it is apparent that there is some barrier to the reaction of activated aromatic radical cations with NO<sub>2</sub> in the gas phase, the origin of this barrier is not now clear.

### Conclusion

We have studied the gas phase chemistry of aromatic radical cations and that of nitronium ion. Under nonsolvated conditions, nitronium ion plays no part in the nitration mechanism. Rather, nitronium ion gives only O<sup>+</sup> or e<sup>-</sup> transfer. Aromatic radical cations will add NO<sub>2</sub> to give a nitroaromatic product that has been confirmed to be a  $\sigma$ -complex. Nitrosations of aromatic radical cations by reaction with NO give only a  $\pi$ -complex. This is the first clear example of a reaction of an aromatic radical cation with NO<sub>2</sub> to give a nitroaromatic product. This work affirms that aromatic radical cations are a plausible intermediate in the mechanism for aromatic nitration.

Acknowledgment

We acknowledge the generous support of the Army Research Office,  
Contract No. DAAG29-80-C-0046, for this work.

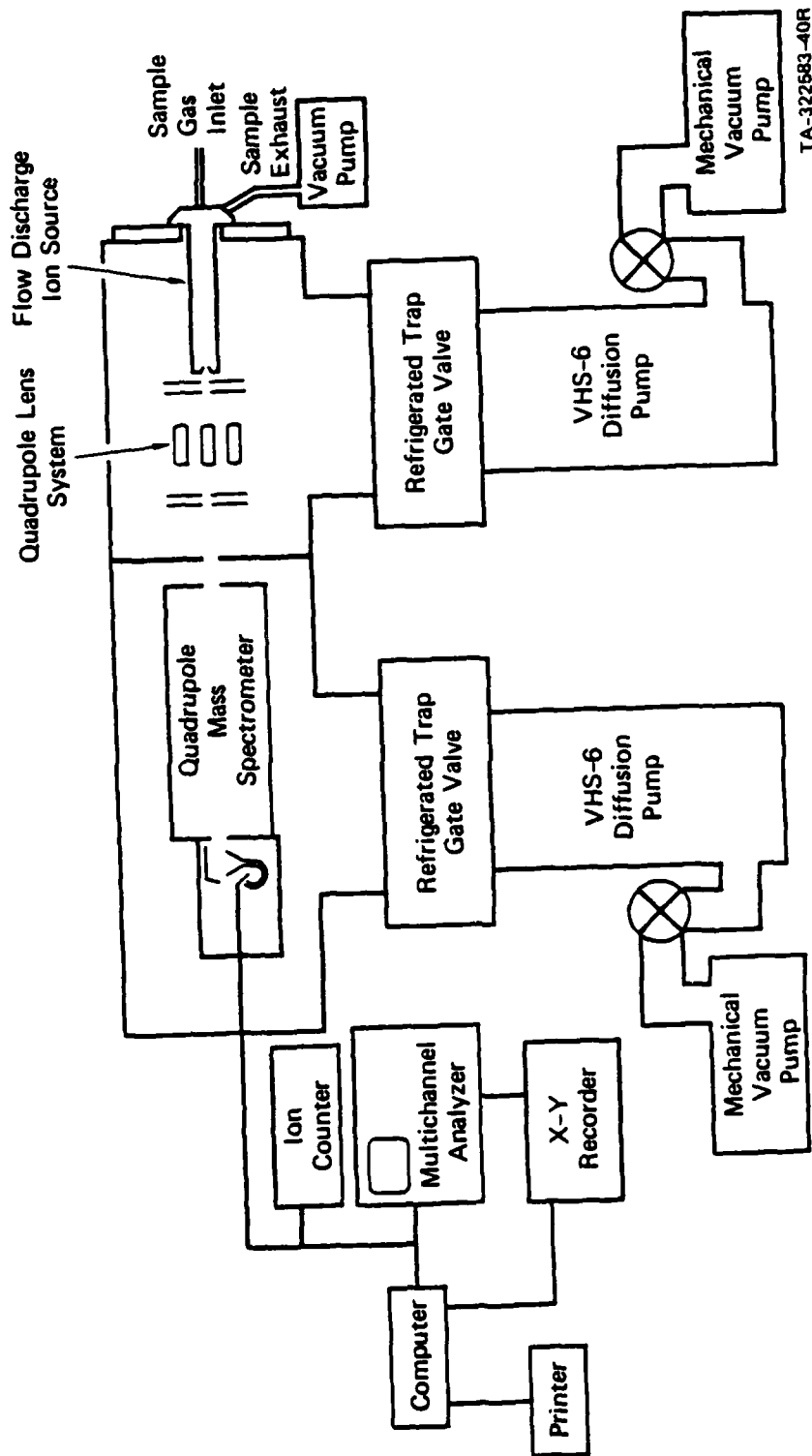
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- Figure 4: Time Dependent Plot of Benzene Dimerization
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TA-322683-40R

FIGURE 1 SCHEMATIC OF FLOW DISCHARGE MASS SPECTROMETER

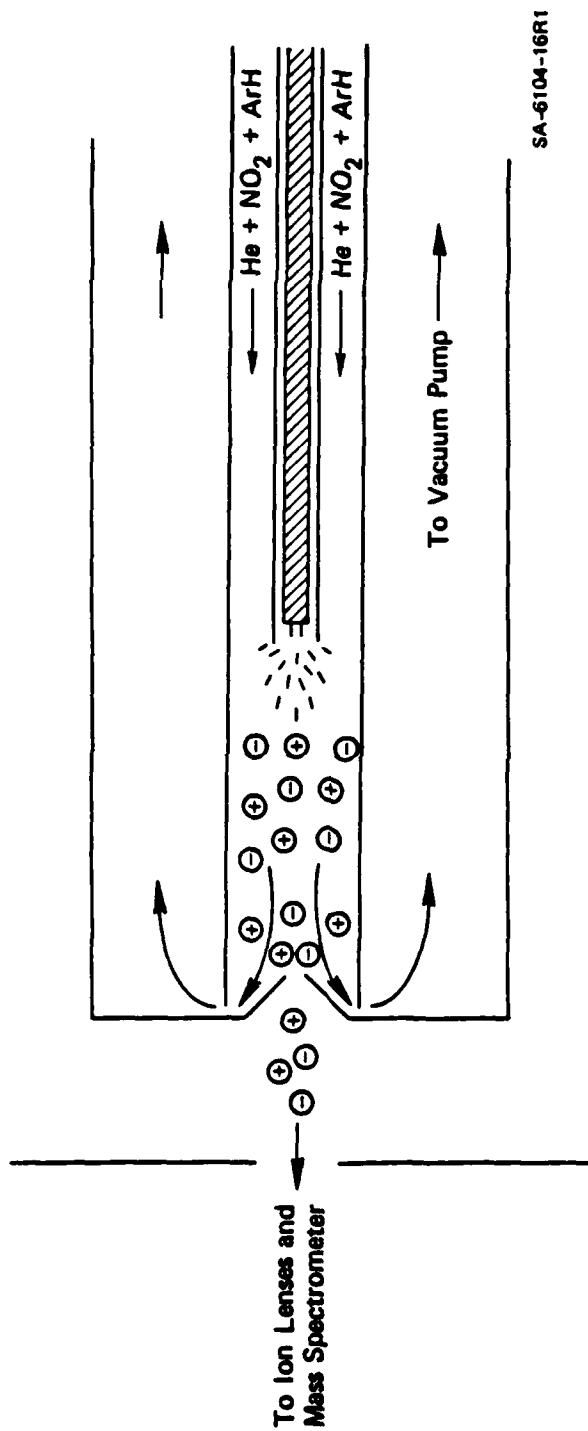
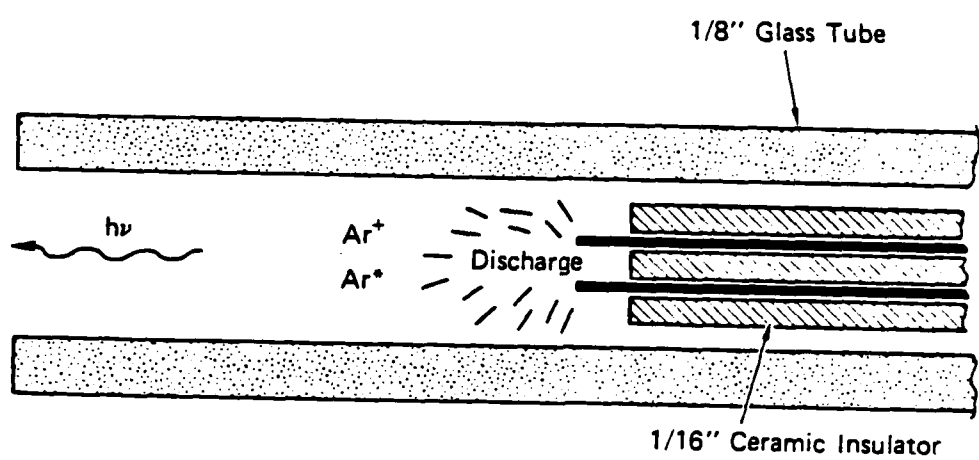
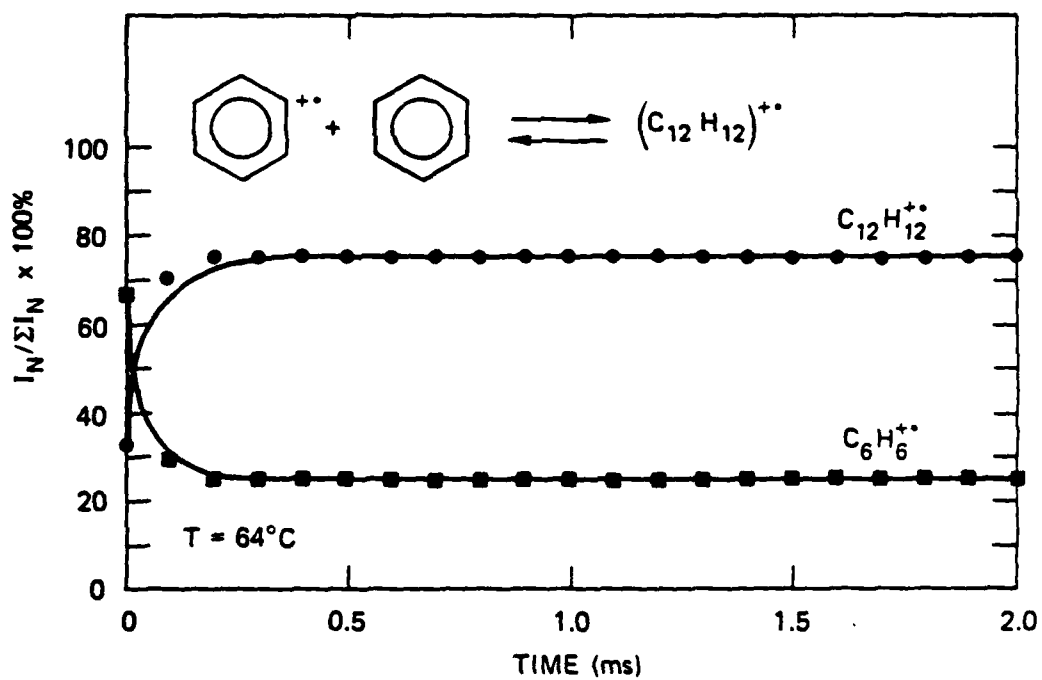


FIGURE 2 SCHEMATIC OF FLOW DISCHARGE ION SOURCE



JA-1152-14A

FIGURE 3 SCHEMATIC OF IONIZER REGION



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FIGURE 4 TIME-DEPENDENT PLOT OF BENZENE DIMERIZATION

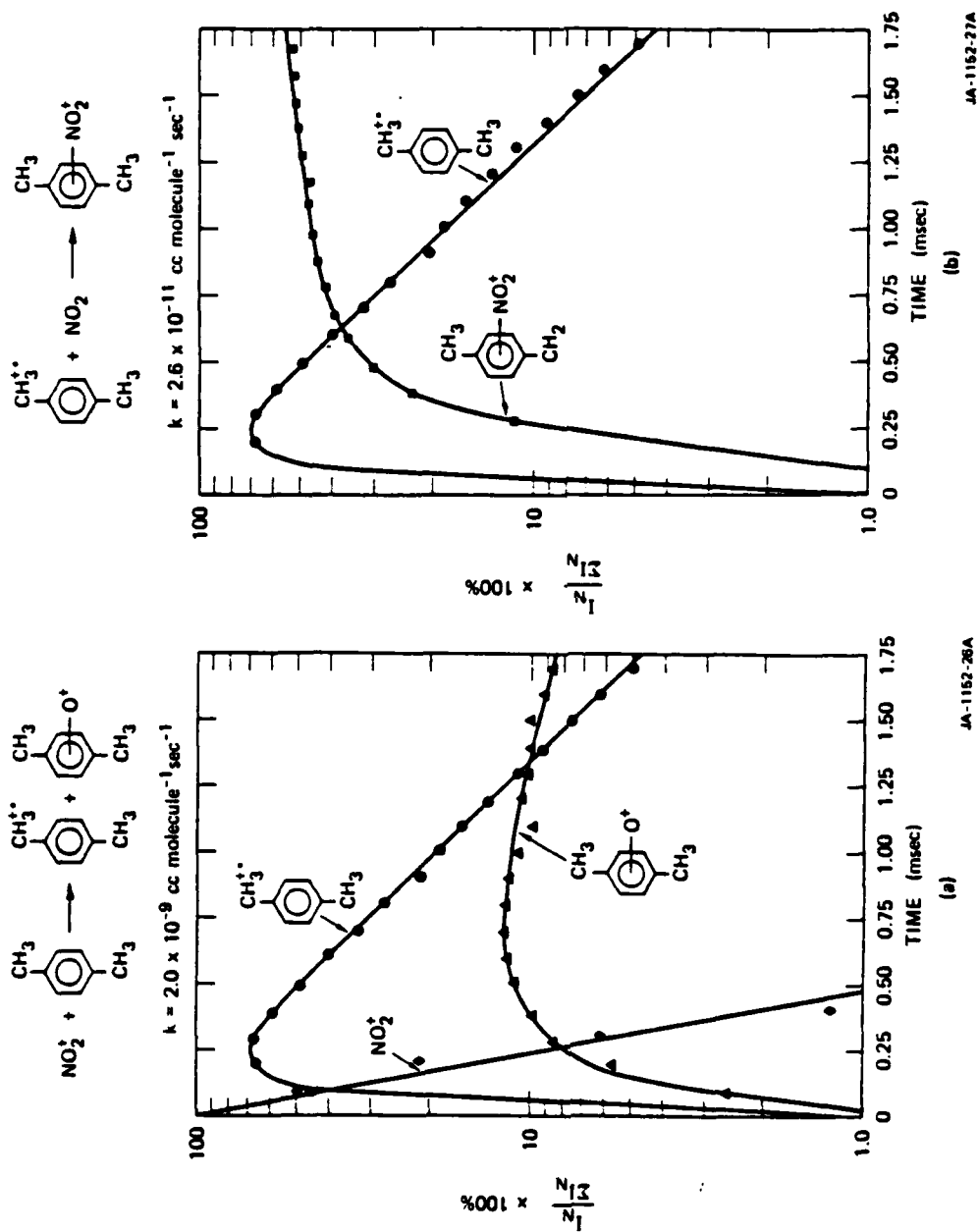


FIGURE 5 TIME-RESOLVED PLOTS SHOWING THE REACTION OF (a) NITRONIUM ION WITH  $p$ -XYLENE, AND (b)  $p$ -XYLENE RADICAL CATION WITH  $\text{NO}_2$

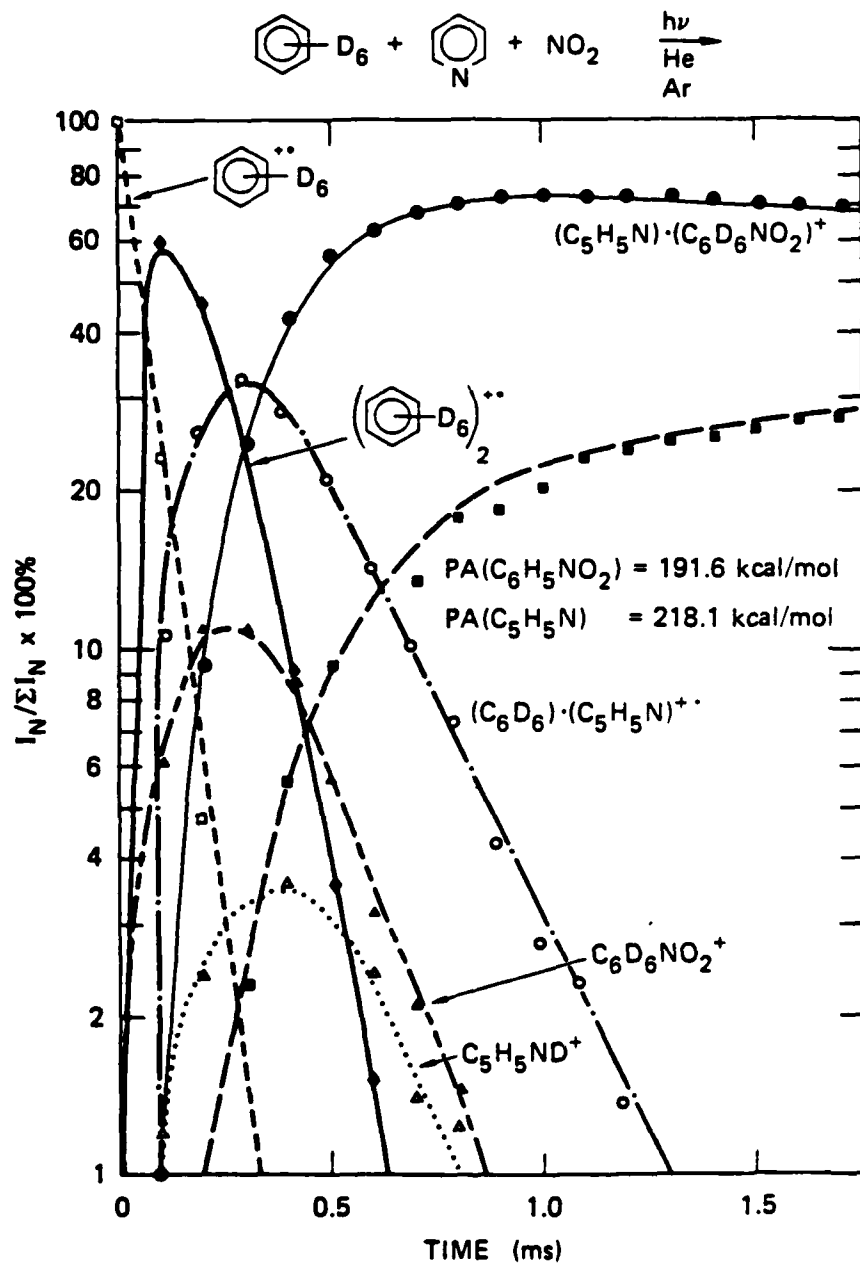


FIGURE 6 RESOLVED MASS SPECTRA OF BENZENE- $d_6$ , PYRIDINE AND  $\text{NO}_2$

## Appendix G

**On the Mechanism of Oxidation of *p*-Nitrosophenol by Nitric Acid. A Labelling Study shows the Proposed Nitrodenitrosation Mechanism to be Untenable†****David S. Ross,\* Ripudaman Malhotra, and Walter C. Ogier***SRI International, Menlo Park, CA 94025, U.S.A.*

Oxidation of *p*-nitrosophenol by  $^{15}\text{N}$ -labelled nitric acid in 34% sulphuric acid (4.4 M) did not produce labelled *p*-nitrophenol, thereby showing the nitrodenitrosation scheme of Bazanova and Stotskii to be untenable; furthermore, the order of the oxidation in nitric acid is 0.67, not 1, as reported by earlier workers.

Oxidation of *p*-nitrosophenol by nitric acid has been the subject of many kinetic studies.<sup>1-4</sup> The reaction exhibits different kinetic forms under different conditions and also shows an induction period of up to 5 min, which is correctly understood in terms of an accumulation of nitrous acid (or possibly other  $\text{N}^{\text{III}}$  species). Addition of  $\text{N}^{\text{III}}$  shortens or eliminates the induction period. The rate of reaction is markedly affected by the acidity of the medium the rate being maximum at ca. 60% sulphuric acid. Several different mechanisms have been pro-

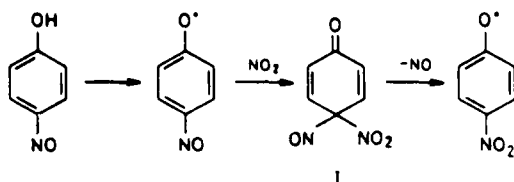
posed for the oxidation, but they have all invoked  $\text{NO}_2$  or  $\text{N}_2\text{O}_4$  ( $\text{N}^{\text{IV}}$ ) as the reactive species.<sup>1-4</sup> Bazanova and Stotskii recently published a detailed analysis of the reaction and presented a mechanism consistent with most facts.<sup>3,4</sup> An important step in their scheme was the formation of an intermediate quinolide (I) via ring attack by  $\text{NO}_2$ , followed by homolytic loss of  $\text{NO}$  to give *p*-nitrophenol (Scheme 1).

As a test of this proposed scheme, we performed a study of the oxidation with  $^{15}\text{N}$ -labelled nitric acid and with sufficient  $\text{N}^{\text{III}}$  present (unlabelled) to avoid the induction period. The intermediacy of a species such as I would result in the formation of labelled product nitrophenol.

We prepared fresh solutions of 0.10 M  $\text{H}^{15}\text{NO}_3$  (>99%  $^{15}\text{N}$ )

† For Part 2 of the series 'Studies on Aromatic Nitration,' see D. S. Ross, K. F. Kuhlmann, and R. Malhotra, *J. Am. Chem. Soc.*, submitted for publication.





Scheme 1

and  $1.59 \times 10^{-3}$  M HONO in 34% sulphuric acid with appropriate sodium salts.<sup>‡</sup> The solutions (at 27 °C) were then adjusted to  $1.00 \times 10^{-2}$  M in *p*-nitrosophenol and held for 270 s, during which period 75% of the starting nitroso-compound was converted into the product, nitrophenol.

Mass spectral analysis of the recovered product showed incorporation of  $^{15}\text{N}$  to be negligible, <2%; thus in 34% sulphuric acid, a nitrodenitrosation scheme does not operate. This result is similar to that obtained in the labelling experiments of Bonner and Hancock<sup>7</sup> for the oxidation of 2,5-dimethylnitrosobenzene in carbon tetrachloride by added  $\text{N}^{\text{IV}}$ . These authors established further that the oxidation was first order in  $\text{NO}_2$  (and therefore half order in  $\text{N}_2\text{O}_4$ ) and that it is most likely that an oxygen transfer from  $\text{NO}_2$  to the nitroso group occurs.

In aqueous acid neither  $\text{NO}_2$  nor  $\text{N}_2\text{O}_4$  is present in anything but very small concentrations, and it is not possible to work directly with the  $\text{N}^{\text{IV}}$  species in such an environment. The order of the reaction, however, in nitric acid can suggest the order in  $\text{NO}_2$ . Our data over a range of nitric acid concentrations in 40%  $\text{H}_2\text{SO}_4$  are given in Figure 1.

The observed slope is 0.67, which is in not in agreement with the results of Ogata and Tezuka,<sup>1</sup> Granzow and Wilson,<sup>2</sup> and Bazanova and Stotskii.<sup>3,4</sup> All accounts, in dioxan and in sulphuric acid, claim a first-order dependence in nitric acid.

However these reports are not without problems. Ogata and Tezuka established the first-order behaviour in dioxan by using nitric acid as both their acid and the source of  $\text{N}^{\text{V}}$ . They then corrected the observed rate constants for the acidity dependence component of the rate. This procedure obscures the full role of nitric acid and cannot be trusted to provide a clear order. Granzow and Wilson, for their work in sulphuric acid, did not show any data for the aspect of the work dealing with the order in nitric acid, merely providing a statement of first-order behaviour. Bazanova and Stotskii provide data

<sup>‡</sup> The  $\text{N}^{\text{III}}$  species most prevalent in 34% sulphuric acid is HONO; however we cannot rule out some small quantities of  $\text{N}_2\text{O}_3$  as being kinetically important.<sup>3,4</sup> For the purposes of the discussion here we will use the full quantity of  $\text{NaNO}_2$  added to the reaction medium in terms of molecular nitrous acid.

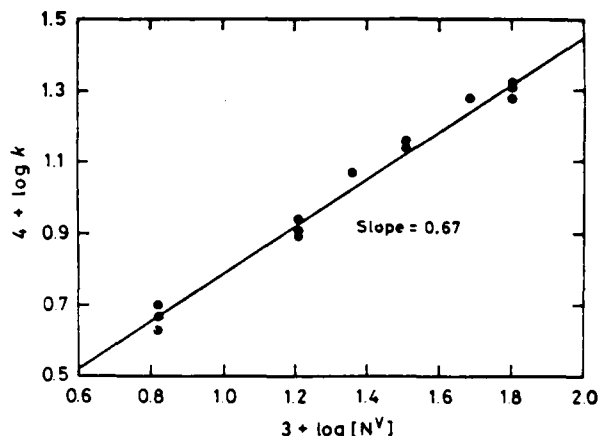


Figure 1. Variation of the pseudo first-order rate constant for oxidation of *p*-nitrosophenol in 40%  $\text{H}_2\text{SO}_4$  with nitric acid concentration.

that show a first-order dependence in nitric acid but over a very narrow range of nitric acid concentrations ( $0.9\text{--}1.9 \times 10^{-2}$  M) in 40% sulphuric acid. We thus stand by our conclusion that in 40% sulphuric acid, at least, the order is 0.67.

The order of the developed reaction in *p*-nitrosophenol is unity as observed by the previous investigators. Furthermore, nitrous acid is the product of the reaction, and its concentration changes manyfold during the reaction. Yet the disappearance of *p*-nitrosophenol is first order. It may therefore be concluded that the developed reaction is zero order in nitrous acid.

The observed order of oxidation in the various reactants can not be reconciled with a simple scheme, and we are currently working on the details of the mechanism. We can, however, safely conclude that the mechanism is more complex than reported by earlier investigators, and definitely does not proceed via nitrodenitrosation.

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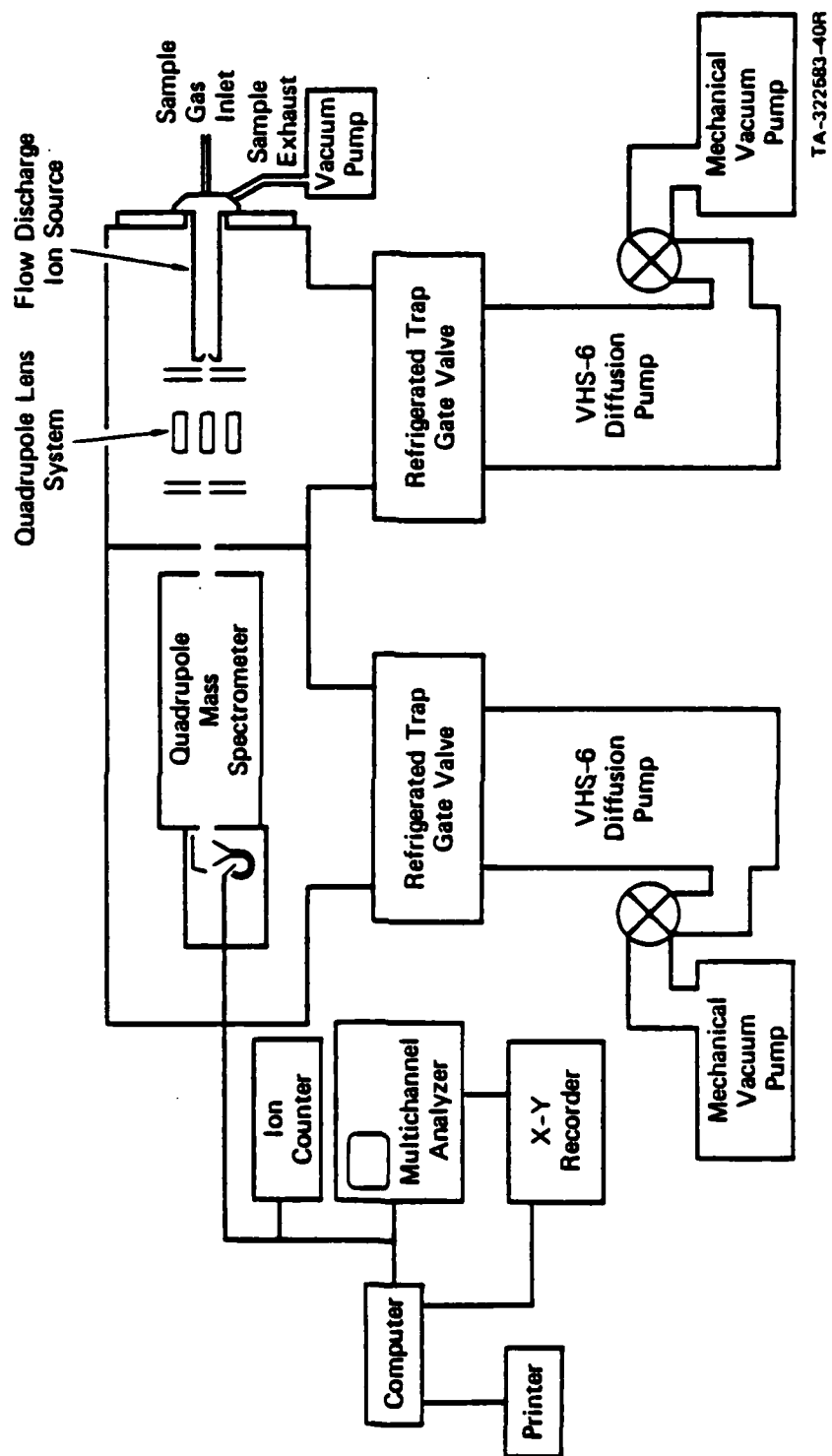
## Appendix H

### A SIMPLE HIGH PRESSURE FLOW TUBE FOR ION-MOLECULE STUDIES

By: Robert J. Schmitt, and S. E. Buttrill, Jr.  
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We have developed a simple high pressure flow tube type ion source for a quadrupole mass spectrometer.<sup>1</sup> This source is useful over a wide range of temperatures and pressures for the study of ion-molecule reactions using an open-ended argon flash lamp for photoionization. A schematic of the mass spectrometer is shown in Figure 1, a drawing of the ion source in Figure 2, and the details of the open-ended argon flash lamp that is used as the ionizer in Figure 3. This source has been operated from 5 to 100 torr and from 25° to 200°C. Helium is employed as the carrier/buffer gas, constituting over 95% of the total gas flow. The helium is used to thermalize the newly formed ions by multiple collisions. The source pressure is changed by introducing more helium or by throttling the exhaust flow from the ion source before the vacuum pump (Leybold-Heraeus, 200 L s<sup>-1</sup>). The helium/reactive neutral mixture is resistively heated as it enters the ion source, and this mixture is pumped back past the outside of the flow tube to help maintain a constant source temperature.

The argon flash lamp is constructed from an open ended 1/8-inch-OD Pyrex tube into which a 1/16-inch-OD, two-hole ceramic insulator has been inserted. Two 5/1000-inch molybdenum electrodes are inserted in the insulator; they protrude about 1/16-inch beyond the end of the insulator and are 1/8-inch from the opening of the glass tubing. A steady flow of argon representing about 0.5 torr of the total pressures is maintained through the Pyrex tube. The lamp is pulsed at 100 Hz and at a potential of 2500 V from an HP 6516A power supply. The pulse rate



TA-322583-40R

FIGURE 1 SCHEMATIC OF FLOW DISCHARGE MASS SPECTROMETER

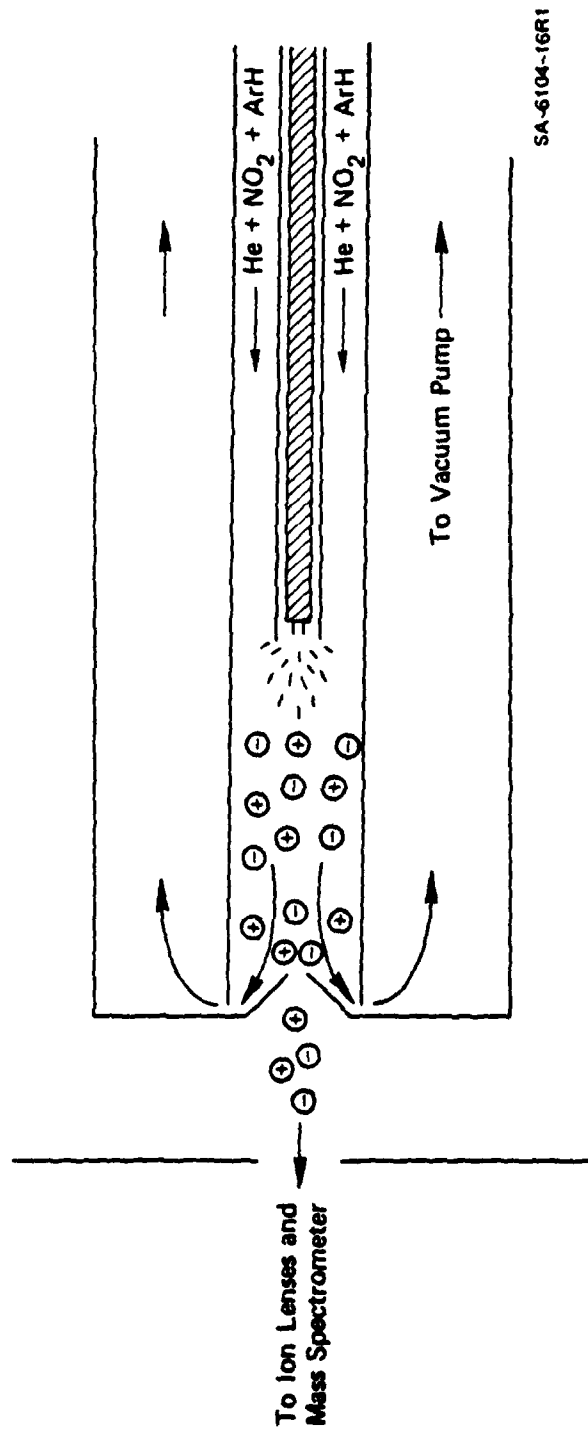
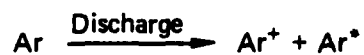
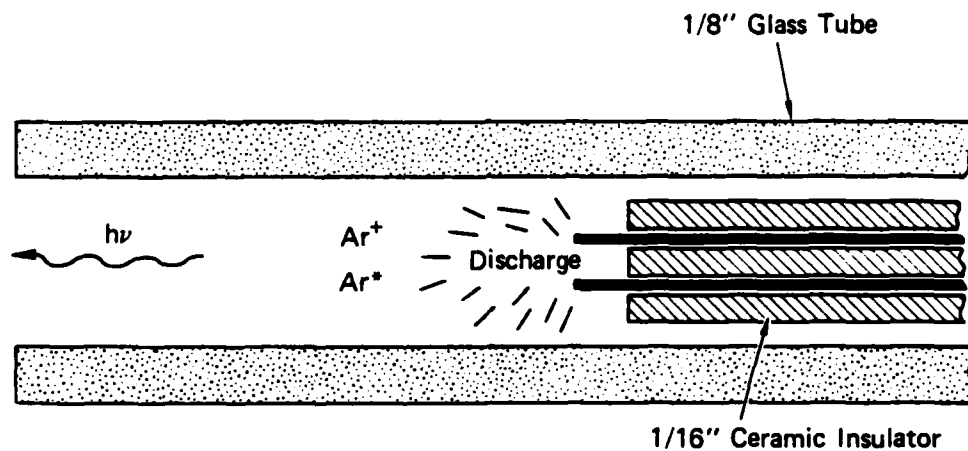


FIGURE 2 SCHEMATIC OF FLOW DISCHARGE ION SOURCE



$$h\nu = 11.83 \text{ eV and } 11.62 \text{ eV}$$

$Ar^+$  is lost due to collision with the walls

No ions will be formed from any neutral where  $IP(\text{Neutral}) > 12 \text{ eV}$

JA-1152-14

FIGURE 3 BLOWUP OF IONIZER REGION

is regulated by an air spark gap. The discharge in argon produces both  $\text{Ar}^+$  ions and argon metastables. The ions are lost to the walls, but the metastables emit 11.83 and 11.63 eV photons, which ionize anything with an IP of less than 11.8 eV down the length of the flow tube. Hence, a plug of gas from the end of the Pyrex tube to the sampling orifice is ionized and is then sampled through a 100  $\mu\text{m}$  pinhole orifice, and the mass spectrum with respect to time is recorded by the computer. Pseudo-first-order rate constants can be calculated. The Pyrex tube shields the reactive neutrals in the helium from the high energy discharge, thus diminishing or eliminating decomposition of the starting materials.

A helium concentration of  $10^{17}$  molecules  $\text{cm}^{-3}$ , a reactive neutral concentration of  $10^{13}$  molecules  $\text{cm}^{-3}$ , and an ion density of  $10^8$   $\text{cm}^{-3}$  are the normal operating conditions. The maximum ion residence time is 5 ns.

This very simple, yet highly versatile ion source is being used to study ion-molecule reactions at high temperatures. The ion source combines pressure and temperature variability over a wide range with ease of construction.

#### References

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Appendix I

FOURIER TRANSFORM NMR OF TWO-SITE CHEMICAL EXCHANGE SYSTEMS:  
EXPERIMENTAL LIMITATIONS OF DETERMINATION OF RATE

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ABSTRACT

Experimental evidence is provided that confirms the nonexponential decay of the nmr signals in chemically exchanging systems. Consequently, receiver dead time can significantly alter the rate data obtained by line shape analysis of FT nmr signals.

FOURIER TRANSFORM NMR OF TWO-SITE CHEMICAL EXCHANGE SYSTEMS:  
EXPERIMENTAL LIMITATIONS OF DETERMINATION OF RATE

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The time delay between the end of the transmitter pulse and the activation of the receiver (receiver dead time) can significantly alter the rate data obtained by line shape analysis of FT nmr signals. It is well known that the free induction decay (FID) resulting from applying of a radio frequency (rf) pulse to an ensemble of nuclear spins in a magnetic field follows a simple exponential decay with time constant  $T_2$ , the spin-spin relaxation time. For a two-site system undergoing chemical exchange, the solution to Bloch equations for the X and Y components of magnetization in the rotating frame is given by equation 1:<sup>2</sup>

$$G(t) = C_1 e^{\Lambda_1 t} + C_2 e^{\Lambda_2 t} \quad (1)$$

where the real part of the solutions for  $\Lambda_1$  and  $\Lambda_2$  are<sup>3,4</sup>

$$\Lambda_{1,2} = -A_2 \pm \left\{ \frac{G + (G^2 + H^2)^{1/2}}{2} \right\} \quad (2)$$

in which

$$G = \left( \frac{1}{T_{2A}} - \frac{1}{T_{2B}} \right)^2 / 4 + \frac{1}{T_A T_B} - \frac{\Delta\omega_{AB}^2}{4} \quad (3)$$

$$H = \left( \frac{1}{T_{2A}} - \frac{1}{T_{2B}} \right) \Delta\omega_{AB} / 2 \quad (4)$$

$$T_{A(B)} = \text{life time in site A (or B)} \quad (5)$$

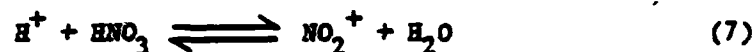


and

$$\frac{1}{\tau_{2A(B)}} = \frac{1}{\tau_{A(B)}} + \frac{1}{\tau_{1A(B)}} \quad (6)$$

Simple inspection of Equation 1 indicates that the decay of the FID for a chemical exchange system is nonexponential, consisting of a sum of two exponentials. Calculations, however, show that  $\Delta_1 = \Delta_2$  when the rate of exchange is lower than or equal to the observed rate at the coalescence point, i.e., the slow exchange region.<sup>5</sup> As the spectrum approaches the fast exchange realm,  $\Delta_1 \neq \Delta_2$  and the decay becomes nonexponential. We wish to report experimental results that do not agree with the above theory near coalescence, i.e.,  $\Delta_1 \neq \Delta_2$  on the slow exchange side.

We first noticed the nonexponential decay below the coalescence point while conducting a study of the nitric acid/nitronium ion equilibrium in aqueous sulfuric acid solutions equation 7.



Acoustic ringing in the probe was giving rise to an undulating baseline. We could eliminate the initial spike in the FID by increasing the receiver dead time. However, as can be seen in Figure 1, this procedure resulted in narrower lines for nitric acid and nitronium ion, implying a slower chemical exchange. The alteration in the signal was real and not an artifact of the phase. One explanation for this unexpected observation was a nonexponential decay of the nmr signal; however, this view is inconsistent with equation 1.

To test this hypothesis we obtained a  $^1H$  nmr spectrum of dimethylformamide at 120°C and 90 MHz. The two methyl resonances were near coalescence. Increasing the receiver dead time to greater than 10 ns, we found a dramatic change in the nmr spectrum (Figure 2). The two poorly resolved resonances split into two relatively sharp signals. Once again, this finding would typically be associated with a much slower rate of chemical exchange.

However, we could not, support our hypothesis on any theoretical grounds, because, as mentioned earlier, analysis of the Bloch equations leads only to a single exponential term when the chemical exchange is slower than the rate at coalescence. Recently, Garroway and Kaplan reported on the nonexponential decay of the nmr signals during chemical exchange.<sup>6</sup> Taken together, our experimental data and their theoretical analysis provide a strong basis for a cautionary note to the practicing nmr spectroscopist. It is suggested that measurement of chemical exchange rates by FT nmr necessarily yields somewhat slower rates. The artifact arises because acquisition of the data is begun only after a certain delay following the pulse, allowing the fast component of the reaction to decay. The effect is in most pronounced when the time constant of the nmr signal is on the order of the receiver dead time. Thus for instruments operating with dead times of about 500  $\mu$ s, the distortion in rate data would be most significant for signals separated by about 600 Hz at 90 Mhz. This circumstance will be encountered a) for nuclei with large chemical shift ranges, b) as higher magnetic fields are used, or c) when receiver dead time is deliberately increased to eliminate undulations in the baseline.

We hope that the readers will take note of this effect and also reexamine some of the earlier work, which, in light of the present discussions, is suspect.

#### Acknowledgment

Support for this work by the United States Army Research Office Contract No. DAAG29-80-C-0046 is gratefully acknowledged.

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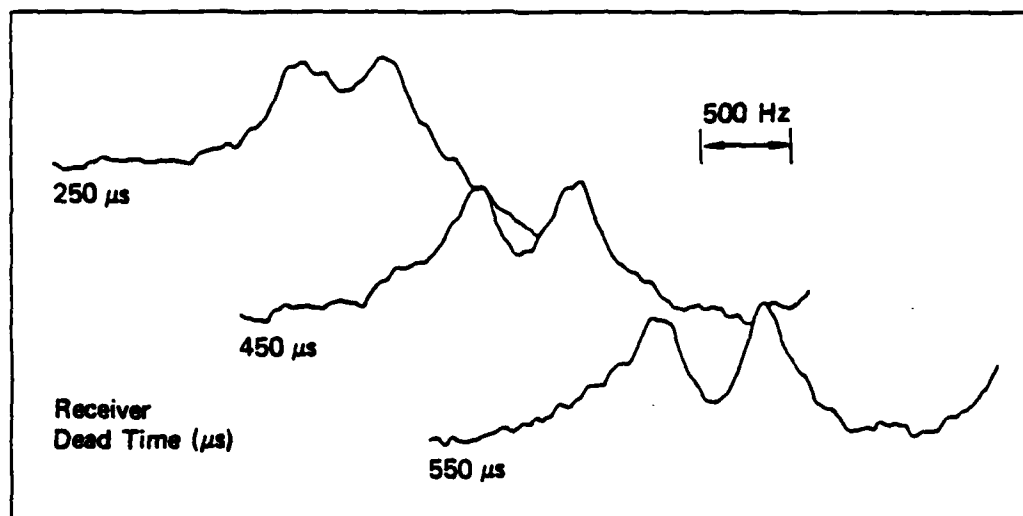
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Figure 1  $^{14}\text{N}$  SPECTRA OF THE NITRIC ACID/NITRONIUM ION RESONANCES OF  
1.0 M  $\text{NH}_4\text{NO}_3$  IN ~89%  $\text{H}_2\text{SO}_4$  OBTAINED ON A JEOL FX-90Q (II) nmr  
SPECTROMETER OPERATING AT 6.47 MHz

The spectra were acquired as a function of the receiver dead time. Experimental conditions - probe temperature was 30°C; number of transients per spectrum was 10,000; acquisition time was 45.9 ms. Internal  $\text{D}_2\text{O}$  was used for the field-frequency lock.

Figure 2  $^1\text{H}$  SPECTRA OF THE METHYL RESONANCES OF 80% DMF IN  $\text{CDCl}_3$   
OBTAINED ON A JEOL FX-90Q (II) nmr SPECTROMETER OPERATING AT  
89.60 MHz

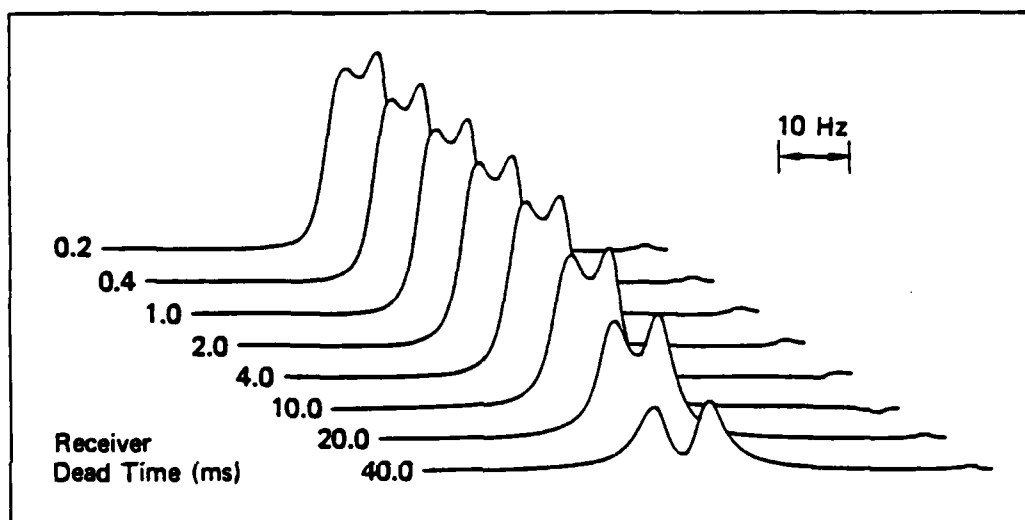
The spectra were acquired as a function of the receiver dead time. Experimental conditions - probe temperature was 120°C; number of transients per spectrum was 8; acquisition time was 4.14 s.



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FIGURE 1  $^{14}\text{N}$  SPECTRA OF THE NITRIC ACID/NITRONIUM ION RESONANCES OF  $1.0\text{ M NH}_4\text{NO}_3$  IN  $\sim 89\% \text{ H}_2\text{SO}_4$  OBTAINED ON A JEOL FX-90Q (II) nmr SPECTROMETER OPERATING AT  $6.47\text{ MHz}$

The spectra were acquired as a function of the receiver dead time. Experimental conditions — probe temperature was  $30^\circ\text{C}$ ; number of transients per spectrum was 10,000; acquisition time was 45.9 ms. Internal  $\text{D}_2\text{O}$  was used for the field-frequency lock.



JA-327583-48

**FIGURE 2**  $^1\text{H}$  SPECTRA OF THE METHYL RESONANCES OF 80% DMF IN  $\text{CDCl}_3$  OBTAINED ON A JEOL FX-90Q (II) nmr SPECTROMETER OPERATING AT 89.60 MHz

The spectra were acquired as a function of the receiver dead time.  
Experimental conditions — probe temperature was  $120^\circ\text{C}$ ; number of transients per spectrum was 8; acquisition time was 4.14 s.

## Appendix J

### EXPERIMENTAL PROCEDURE FOR FLASH PHOTOLYSIS EXPERIMENTS

These experiments for generating and detecting aromatic radical cations use a standard laser flash photolysis system with a perpendicular probe-excitation arrangement. A Lambda Physik EMG 500 excimer laser is used as the light source. The laser is operated on Kr/F2 to obtain emission at 249 nm and on Xe/F2 to obtain emission at 350 nm. The excimer laser has a pulse length between 12 and 20 ns. The transient absorption of aromatic radical cations transient absorption is measured using an Oriel 1000-W tungsten halogen incandescent lamp operated in cw mode.

A Hamamatsu R928 photomultiplier with its last diode modified to obtain fast response and high peak currents for short times is used as the detector for the transient radical cations. The photomultiplier is gated by a 10-15 V gating pulse from an HP 214A pulse generator (master trigger) for a duration of 100 to 140  $\mu$ s; 60 to 80  $\mu$ s after the gating pulse turns on the photomultiplier, a second pulse generator (HP 214A0 triggers the laser. A fast timing amplifier is used to multiply the output signal five times. The output is displayed on a TEK 7844 (500 MHz) oscilloscope with a 50  $\Omega$  terminator. The oscillographic trace is photographed by a fast camera.

The solvent used in the experiments is either acetonitrile or methylene chloride, which has been fresh distilled and dried to remove the water. The aromatic concentration and the nitrogen dioxide concentration are measured by an HP 8450A UV-Vis spectrophotometer. Acetonitrile is not generally used because it cannot be dried enough to eliminate all of the water. The nitrogen dioxide and aromatic concentrations are generally kept at  $10^{-3}$  M. The nitroaromatic products

are analyzed on an IBM model 9533 HPLC equipped with a variable wavelength UV detector.



## Appendix K

### DISTRIBUTION OF $\text{NO}_x$ IN AQUEOUS ACID SYSTEMS

David S. Ross and Chee Liang Gu

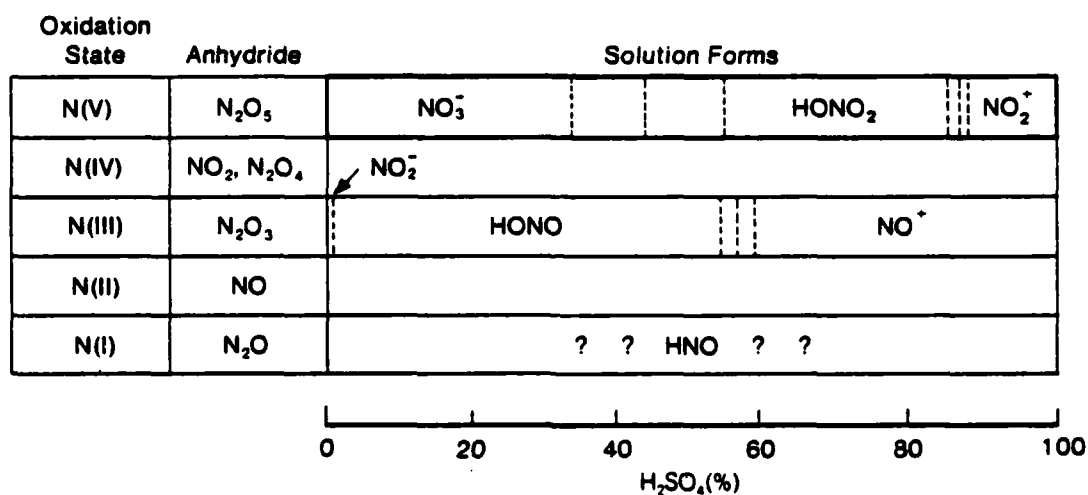
The forms of the oxyacids of nitrogen both in the gas phase and the condensed phase are shown in Figure 1. The four oxidation states we will be concerned with here are II through V. It was of interest to establish how the different oxidation states would be distributed over the range of acids studied.

Accordingly, we performed a series of experiments in which 100 torr of  $\text{NO}_2$  (0.64 mmol) was rapidly stirred in a 212-ml reaction flask at  $25^\circ\text{C}$  with 50 ml of various strengths of sulfuric acid both in the absence and presence of oxygen. The final equilibrium positions of the system were attained.

The results for the  $\text{O}_2$ -free work are presented in Figure 2. The distributions are widely varying and obviously a significant function of the acidity of the medium. Nitrate,  $\text{NO}$ , and nitrous acid are prominent up to 20% sulfuric acid, with the production of molecular nitric acid from nitrate beginning at that acidity. Nitric acid becomes an increasing fraction of the  $\text{N(V)}$  with increasing acidity.

In the range 50%-70% acid, small quantities of  $\text{NO}_2$  are seen in the gas phase, while  $\text{NO}$  disappears, and  $\text{HONO}$  becomes replaced by  $\text{NO}^+$ . Finally, above 80%  $\text{H}_2\text{SO}_4$ , nitric acid is replaced by its dehydrated form  $\text{NO}_2^+$ . This last observation agrees well with recent literature accounts of the ionization of nitric acid in the same region of acidity.<sup>1</sup>

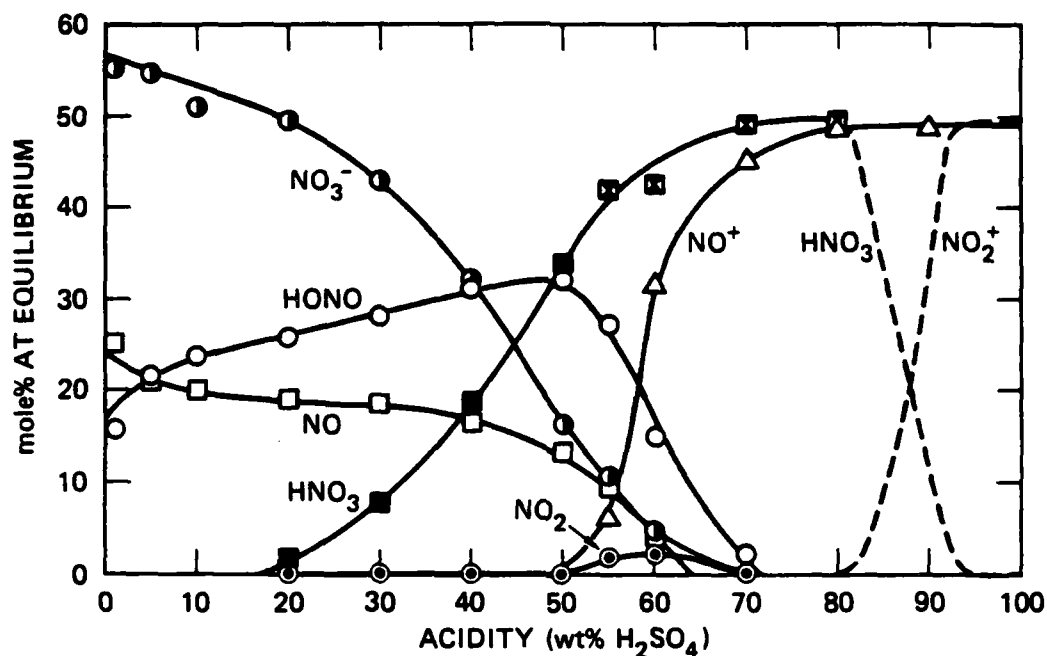
The seemingly complex behavior of the system can be explained rather simply. Recognizing that  $\text{NO}_3^-$ ,  $\text{HNO}_3$  and  $\text{NO}_2^+$  are all  $\text{N(V)}$  species, inspection of Figure 1 makes it clear that the  $\text{N(V)}$  content of the equilibrium mixture remains fairly constant over the entire acid range at 50%-60%. Thus we can reasonably presume that the first event after dissolution of the  $\text{N(IV)}$  in the acid medium is disproportionation,



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FIGURE 1 DISTRIBUTION OF THE POSITIVE OXIDATION STATES OF NITROGEN IN ACIDIC MEDIA

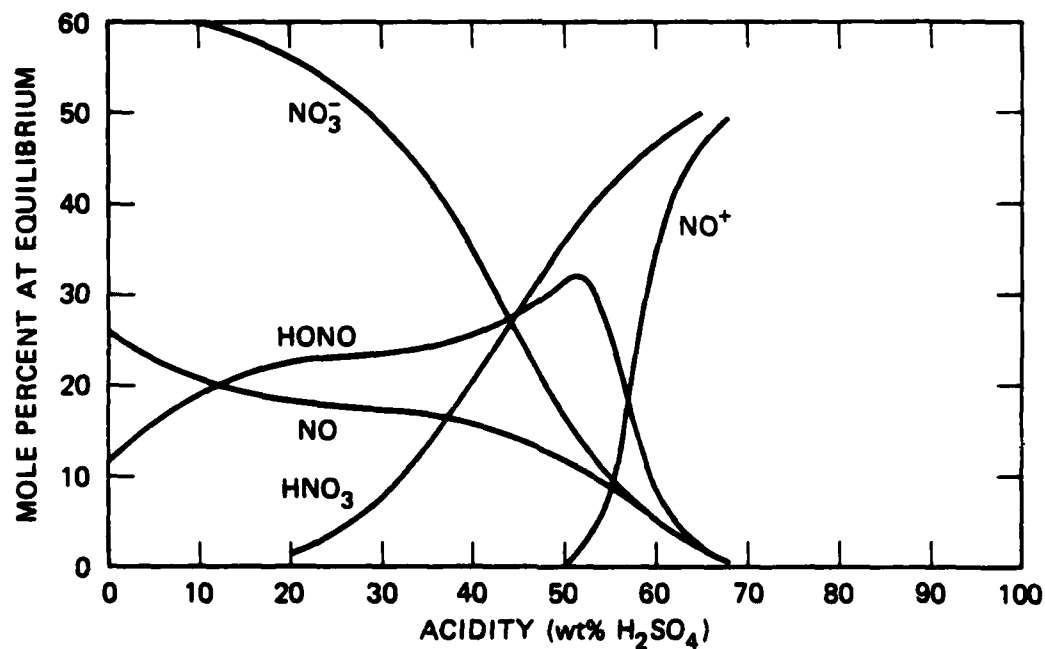
The dashed, vertical lines are for the 25, 50, and 75% points of conversion.  
 The data for N(V) are from N. Deno, H. Peterson, and E. Sacher, J. Phys. Chem., 65, 199 (1961). The data for N(III) are from N. Bayliss et al., Aust. J. Chem., 16, 933 (1963).



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FIGURE 2 EQUILIBRIUM PROFILES FOR NO<sub>x</sub> SPECIES VERSUS ACIDITY

(○ HONO; □ NO; ● NO<sub>3</sub><sup>-</sup>; ■, ■ HNO<sub>3</sub>; ● NO<sub>2</sub>; △ NO<sup>+</sup>; --- from literature; Reference 13. Almost all the data points were determined by direct measurement; the four HNO<sub>3</sub> points (■) were established by difference. The NO and NO<sub>2</sub> are in the gas phase, and all other species are in the condensed phase.



JA-327583-31

FIGURE 3 PREDICTED DISTRIBUTION ON THE BASIS OF  $2\text{NO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_3 + \text{HONO}$  AND  $3\text{HONO} \rightleftharpoons 2\text{NO} + \text{H}_2\text{O} + \text{HNO}_3$

Acids ionized on the basis of discussion in text.

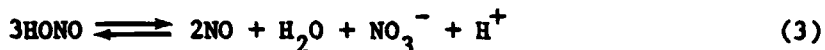


followed by ionization of the two product acids depending on the acidity.



The four ionization equilibria effective here are (Equilibrium 2c is included for completeness, although it is unimportant at acidities greater than pH 3.4, at which point the N(III) is converted to HONO. Most of our studies were performed at higher acidities, where nitrite concentrations were not significant.) So there are initially established equimolar quantities of N(III) and N(V).

Next, below 60%  $\text{H}_2\text{SO}_4$  where HONO is dominant, the decomposition of nitrous acid becomes significant, and a second equilibrium then becomes important



As the acidity is increased, we would accordingly expect a shift to the left, with NO and N(V) consumed and the concomitant formation of increasing quantities of HONO.

These relationships bring all the observed species up to 60% acid into consideration, and this model for the  $\text{NO}_x$  distribution up to that acidity is confirmed in Figure 3. The figure was synthesized by using equilibria (1) and (3), in which both nitrous and nitric acids are un-ionized, combined with our experimental data for equilibrium NO levels. Equilibrium (1) was presumed to be established fully to the right, and the stoichiometry of (3) was then applied, fixing the mole fraction of NO at a series of observed values. Finally, the HONO and  $\text{HNO}_3$

quantities thereby obtained were broken down into  $\text{HONO}/\text{NO}^+$  and  $\text{HNO}_3/\text{NO}_3^-$  fractions in accord with the data, respectively, of Bayliss et al.<sup>2</sup> and Deno et al.<sup>3</sup>

The agreement of the synthesized model with the experimental observations is surprisingly good, and it is clear that only the two equilibria in (1) and (3) along with the acid/base chemistry in (2) are required to explain the features of most of the system up to 60% sulfuric acid. The behavior of the system at greater acidities is readily explained by Eqs. (2b) and (2c), and thus the distribution over the full range of acidity is understood.

Thus as described above, increasing acidity drives Eq. (3) to the left, increasing the HONO and consuming NO. The increased acidity also protonates nitrate, and molecular nitric acid emerges as  $\text{NO}_3^-$  declines. As the acidity is increased beyond 60%, removal of HONO by ionization to  $\text{NO}^+$  probably completes the consumption of NO, and the HONO is ultimately fully replaced by the cation. Finally, the nitric acid is ionized to nitronium ion,  $\text{NO}_2^+$ .

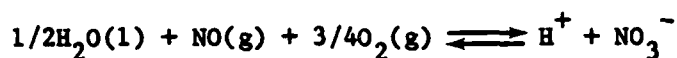
The only feature of the system not explained by the above description is the small quantity of  $\text{NO}_2$  seen in the 60% acid region. This is a curious observation, and it is of interest that at 60%  $\text{H}_2\text{SO}_4$  all the  $\text{NO}_x$  species with oxidation states II through V are present. This region could be a very reactive one, and as we have discussed, the rate of S(IV) oxidation attains its maximum value in that region.

The emergence of some N(IV) in the system can be explained by the fact that only in the 60% region are the molecular (nonionized) forms of HONO and  $\text{HNO}_3$  present together. Thus, Eq. (1) as written must lie at our conditions not fully to the right. At lower acidities,  $\text{HNO}_3$  is converted to nitrate, and Eq. (1) is then driven fully, consuming  $\text{NO}_2$ . When the acidity is increased, however, the ionization of HONO to  $\text{NO}^+$  similarly drives the equilibrium fully to the right, and  $\text{NO}_2$  disappears.

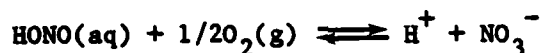
The same series of runs was also made under 1 atm  $\text{O}_2$ . In this case, no NO was seen at any time in the period to equilibrium. The runs

were made only at acidities below 60%  $\text{H}_2\text{SO}_4$ , and here the initial distributions with the exception of NO were seen as noted above for the  $\text{O}_2$ -free runs. However, the ultimate equilibrium was established only after about seven days and was represented by N(V) as the sole product. This observation is consistent with the observations of Pogrebnaya et al.<sup>4</sup> who studied the oxidation of nitrous acid by  $\text{O}_2$  to nitric acid.

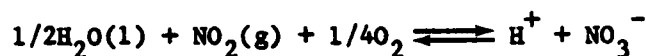
Moreover, our findings are in accord with expectation based on the thermochemistry of  $\text{O}_2/\text{NO}_x$  systems as calculated from available data,<sup>5</sup> in which N(V) is the ultimately favored form of  $\text{NO}_x$  under oxidizing conditions. Thus, at 25°C



$$\log K = 13.7$$



$$\log K = 9.64$$



$$\log K = 7.63$$

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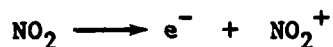
## Appendix L

### ELECTROCHEMICAL PREPARATION OF TNT

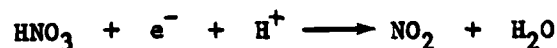
The electrochemical work on this program has been extended to a practical side of nitration chemistry. After Harrar and Pearson<sup>1</sup> showed that  $\text{N}_2\text{O}_5/\text{HNO}_3$  solutions could be prepared electrochemically in an efficient manner, we considered the possibility that these media could be used in the nitration of dinitrotoluene (DNT). Because this work is in progress the results are preliminary, and the discussion serves as a progress report.

Harrar and Pearson showed, that in the anodic compartment of an electrochemical cell,  $\text{NO}_2$  in solution in anhydrous nitric acid could be oxidized to  $\text{N}_2\text{O}_5$ . The cell used  $\text{IrO}_x$  electrodes, and 100%  $\text{HNO}_3$  was used in the cathode. Current efficiencies of about 120% were obtained, and some catalytic activity at the electrode surfaces was presumed to account for the high value. The proposed electrode reactions were

#### anode



#### cathode



To establish first whether  $\text{HNO}_3/\text{N}_2\text{O}_5$  solutions (white fuming nitric acid) were effective in DNT nitration, we performed an experiment in which crystalline  $\text{N}_2\text{O}_5$ , prepared through the  $\text{NO}_2/\text{O}_3$  reaction, was

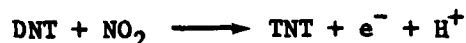


dissolved in anhydrous  $\text{HNO}_3$  to yield a 4.6 M solution. Then 0.33 mmole of 2,6-DNT were dissolved in 2.0 ml of the solution, and the homogeneous system was held at 25°C. The reaction was sampled over several hours, and 2,4,6-TNT was detected as the sole reaction product. It was formed slowly at a rate relative to the starting DNT of about  $1.2 \times 10^{-3}$  %/sec. In a second run with DNT added to anhydrous nitric acid alone, no TNT was observed over the same period.

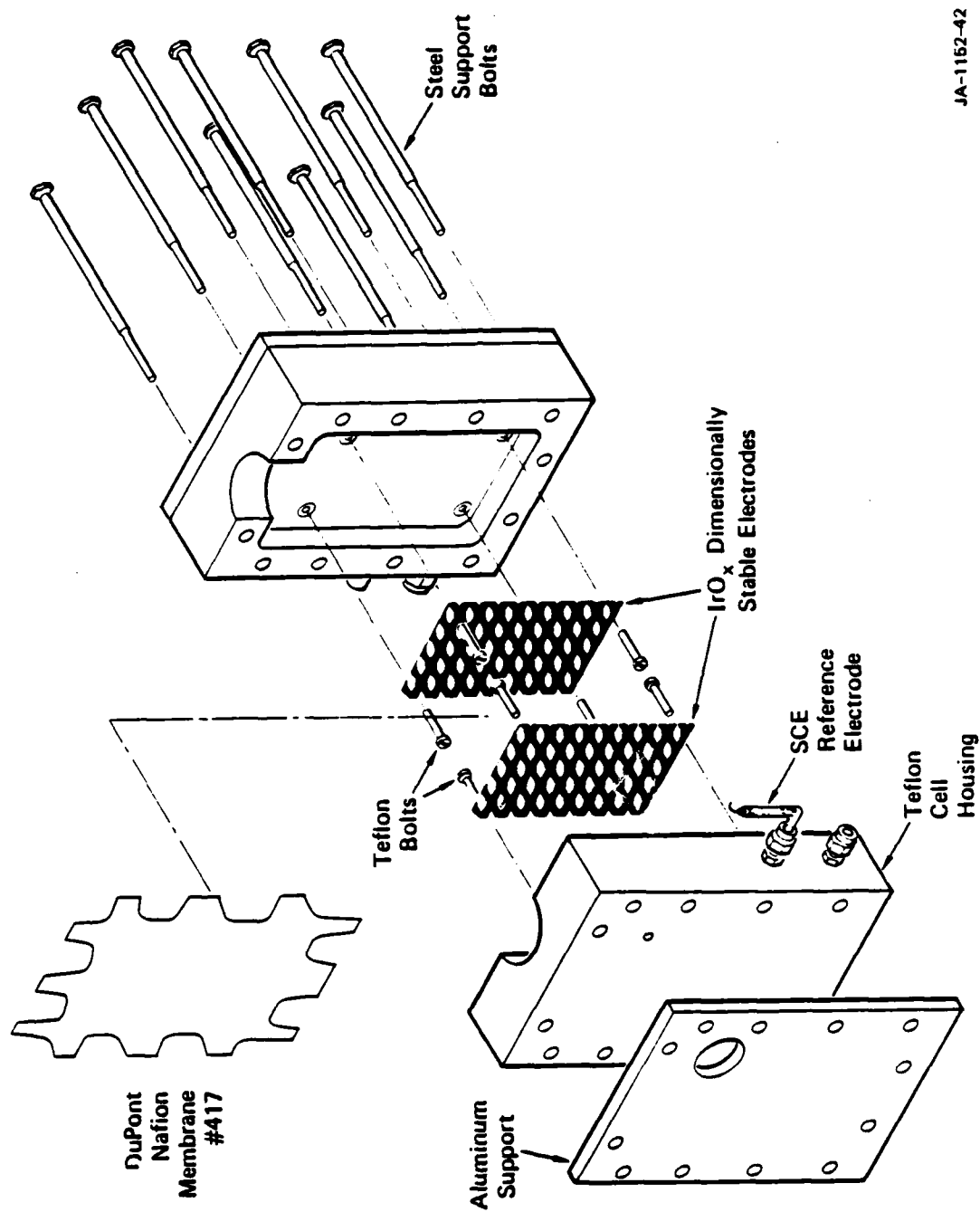
For the electrochemical work to follow, we constructed a cell similar to that used by Harrar and Pearson. Our cell uses  $\text{IrO}_x$  electrodes and a Du Pont Nafion membrane as the separator. A drawing of the cell is shown in Figure 1.

Thirty ml of a saturated solution of  $\text{NO}_2$  in anhydrous nitric acid was placed into the anode compartment, along with 1.10 mmoles of 2,6-DNT. The cell was kept at 25°C. Current was then passed at a potential of 1.4 volts at a rate of 3600 coulombs/hr. The solution was sampled periodically, and TNT was immediately observed as a product by gc analysis. The rate of production of the product was slow, about  $2.0 \times 10^{-3}$  %/sec, based on the starting DNT.

Presently the current efficiency is very low, and further work is proposed to improve the effectiveness of the system. Nonetheless, this finding represents the first synthesis of TNT through the application of electrochemical principles. The overall reaction in the anode compartment yielding TNT is

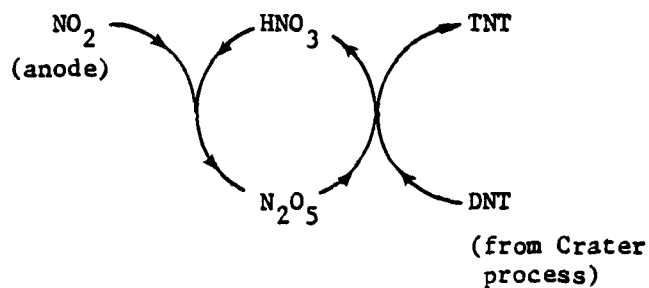


and a TNT synthesis from toluene involving only nitric acid as the reaction medium can be considered. DNT can be produced in an all-nitric acid system, in which toluene is nitrated in 70% acid, and the nitro-toluene then nitrated to DNT in 98% acid.<sup>2</sup> We suggest the following scheme to utilize  $\text{N}_2\text{O}_5/\text{HNO}_3$  chemistry for TNT production.



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FIGURE 1 EXPLODED VIEW OF ELECTROCHEMICAL CELL FOR  $N_2O_6$  PRODUCTION



The advantages of such a process include the elimination of the need for sulfuric acid and the possibility of significantly lower degrees of oxidative side reaction.

Two patent disclosures have been filed dealing with this work.

#### References

1. Harrar, J. E.; Pearson, R. K. J. Electrochem. Soc. 1982, submitted for publication.
2. Crater, W. de C, "The Manufacture of Dinitrotoluene," U.S. Patent 2,362,743, Nov. 14, 1944, assigned to Hercules Power Co.

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